Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2023

Supplementary Information

A new class of third-order nonlinear optical materials: pulse-duration dependent saturable/reverse-saturable absorption and nonlinear refraction in platinum(II) diimine-dithiolate complexes

Dedicated to the memory of Prof. G. C. Papavassiliou

Anna Pintus,[a*] Cristian Pilloni,[a] Gabriele Pippia,[a] Enrico Podda,[a,b] M. Carla Aragoni,[a] Vito Lippolis,[a] Panagiotis Aloukos,[c,d] Dionysios Potamianos,[c,d‡] Nikolaos Chazapis,[c,d] Stelios Couris,[c,d*] George C. Anyfantis,[e] Alexandra M. Z. Slawin,[f] J. Derek Woollins,[f,g] and Massimiliano Arca[a*]

[a] Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, S. S. 554 Bivio per Sestu, 09042 Monserrato, CA, Italy
[b] Centro Servizi di Ateneo per la Ricerca (CeSAR), Università degli Studi di Cagliari, S.S. 554 bivio per Sestu, 09042 Monserrato, CA, Italy
[c] Institute of Chemical Engineering Sciences (ICE-HT), Foundation for Research and Technology-Hellas (FORTH), P.O. Box 1414, 26504 Patras, Greece.
[d] Department of Physics, University of Patras, 26504 Patras, Greece
[e] NanoPhos S.A., PO Box 519, Science and Technology Park of Lavrio, 1st km of Lavrio –Athens Ave., Lavrio 19500, Attica, Greece
[f] EaStCHEM School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, UK, KY16 9ST
[g] Department of Chemistry, Khalifa University, Abu Dhabi 127788, United Arab Emirates.
‡ Present address: Ludwig-Maximilians-Universität München, Am Coulombwall 1, 85748 Garching, Germany.

Contents

1. Tables

Table S1. Crystal data for complexes **1** and **5**.

	1	**5**
Empirical formula	$C_{14}H_{12}N_2PtS_4$	$C_{16}H_{16}N_2PtS_4$
Calculated density (g cm^{-3})	2.360	2.136
Formula Weight	531.59	559.64
μ (mm^{-1})	9.929	8.540
Crystal size (mm^3)	0.21×0.06×0.02	0.30×0.08×0.02
T (K)	125(2)	298(2)
Crystal System	Orthorombic	Monoclinic
Space Group	*Pnma*	$P2_1/c$
a (Å)	7.8675(17)	10.451(5)
b (Å)	14.825(4)	21.309(9)
c (Å)	12.827(3)	8.335(4)
α (°)	90	90
β (°)	90	110.331(16)
γ (°)	90	90
V (Å^3)	1496.1(6)	1740.5(14)
Z	4	4
Z′	0.5	1
Wavelength (Å)	0.71075	0.71073
Radiation type	Mo *K*α	Mo *K*α
Total number of data	8678	37262
Unique reflections	1338	3985
R_{int}	0.0409	0.0542
Parameters	107	210
Restraints	0	0
wR_2 (all data)	0.0657	0.0554
R_1	0.0251	0.0238
GooF	1.131	1.103

Table S2. Selected bond lengths (Å), angles, and dihedral angles (°) for complexes **1** and **5.** Atom labelling scheme as in Figures 1 and S1.

	1		**5**
Pt1-S1	2.2476(12)	Pt1-S1	2.2573(14)
		Pt1-S2	2.2509(13)
Pt1-N1	2.052(4)	Pt1-N1	2.068(4)
		Pt1-N2	2.052(4)
S1-C6	1.761(5)	S1-C13	1.751(5)
		S2-C14	1.746(5)
C6-S2	1.765(5)	C13-S3	1.755(5)
		C14-S4	1.761(5)
S2-C7	1.816(13)	S3-C15	1.815(6)
S2-C7A	1.805(12)	S4-C16	1.792(5)
C6-C6^{i}	1.337(8)	C13-C14	1.345(6)
C7-C7A	1.52(2)	C15-C16	1.506(8)
N1-C5	1.348(6)	N1-C6	1.358(5)
		N3-C7	1.354(6)
C5-C5^{i}	1.474(6)	C6-C7	1.471(6)
N1-Pt1-N1^{i}	79.0(2)	N1-Pt1-N2	79.11(14)
N1-Pt1-S1	95.98(11)	N1-Pt1-S1	96.68(10)
		N2-Pt1-S2	95.44(11)
S2-Pt1-S2^{i}	88.93(6)	S1-Pt1-S2	88.88(5)
N1-Pt1-S1-C6	175.60(3)	N1-Pt1-S1-C13	171.67(4)
		N2-Pt1-S2-C14	175.65(4)
S1-C6-S2-C7	157.9(7)	S1-C13-S3-C15	149.41(5)
S1-C6-S2-C7A	175.2(8)	S2-C14-S4-C16	134.15(4)
C6-S2-S2^{i}-C7^{i}	155.27(7)	C13-S3-S4-C16	123.74(3)
C6-S2-S2^{i}-C7A^{i}	171.10(8)	C14-S4-S3-C15	142.52(5)

Symmetry codes: $^{i} = x, 3/2–y, z$

Table S3. Electrochemical data (V *vs* Fc^+/Fc) recorded by cyclic voltammetry in DMSO for complexes **1**–**6**; scan rate 100 $mV \cdot s^{-1}$).

	$E_{1/2}^{(0/-1)}$			$E_{1/2}^{(+1/0)}$		
	$\lvert E_{pc}-E_{pa}\rvert$	i_{pc}/i_{pa}	$E_{1/2}$	$\lvert E_{pc}-E_{pa}\rvert$	i_{pc}/i_{pa}	$E_{1/2}$
1	0.101	0.82	–1.728	0.081	1.34	–0.177
2	0.120	0.78	–1.678	0.112	0.86	–0.112
3	0.078	0.91	–1.676	0.132	0.79	–0.192
4	0.083	0.85	–1.683	0.128	1.35	–0.072
5	0.126	1.35	–1.778	0.085	0.84	–0.182
6	0.082	1.32	–1.819	0.083	0.79	–0.178

Table S4. UV-Vis absorption maxima λ_{max} (nm) of the solvatochromic absorption band and corresponding molar extinction coefficients ε ($M^{-1} \cdot cm^{-1}$) recorded in DMSO and DMF for complexes **1**–**6**.

	DMSO		DMF	
	λ_{max}	ε	λ_{max}	ε
1	615	4400	623	4500
2	580	4100	593	4200
3	611	4500	626	4600
4	588	5600	598	6700
5	593	4200	605	4300
6	595	5200	602	5300

Table S5. UV-Vis absorption maxima λ_{max} (nm) of the solvatochromic absorption band recorded in different solvents for complexes **1–6**.

	1	**2**	**3**	**4**	**5**	**6**
CH_3CN	604	577	601	581	589	584
DMSO	615	580	611	588	593	595
Acetone	639	603	633	610	614	617
DMF	623	593	626	598	605	602
CH_2Cl_2	645	613	642	614	620	616
$CHCl_3$	667	636	656	634	641	641
THF	686	648	682	654	657	664
Toluene[a]	–	672, 714	–	645, 697	–	703, 750

[a] Spectra could not be recorded in toluene for some complexes due to solubility reasons.

Table S6. Selected experimental bond lengths (Å) and angles (°), corresponding optimised parameters obtained with different functionals and basis sets,[a] for complex **1**; numbering scheme as in Figure S5.

	Structural	mPW1PW			PBE0			B3LYP		
	data	LANL08(f)	CRENBL	Stuttgart	LANL08(f)	CRENBL	Stuttgart	LANL08(f)	CRENBL	Stuttgart
Pt1-S1	2.248	2.265	2.271	2.278	2.262	2.269	2.275	2.290	2.296	2.302
Pt1-S2	2.248	2.263	2.270	2.276	2.261	2.267	2.274	2.288	2.294	2.300
Pt1-N1	2.051	2.039	2.049	2.061	2.036	2.046	2.058	2.066	2.074	2.087
Pt1-N2	2.051	2.039	2.049	2.061	2.037	2.046	2.058	2.065	2.074	2.087
C13-S1	1.761	1.746	1.749	1.748	1.745	1.747	1.747	1.760	1.762	1.762
C12-S2	1.761	1.744	1.747	1.746	1.743	1.745	1.745	1.757	1.760	1.759
C13-S3	1.765	1.759	1.759	1.759	1.758	1.758	1.758	1.773	1.774	1.773
C14-S4	1.765	1.759	1.760	1.759	1.758	1.758	1.758	1.772	1.773	1.772
C11-C12	1.337	1.361	1.360	1.360	1.362	1.361	1.361	1.364	1.363	1.363
C13-C14	1.516	1.514	1.515	1.515	1.514	1.514	1.514	1.521	1.521	1.521
C5-C6	1.474	1.457	1.459	1.465	1.457	1.458	1.461	1.462	1.463	1.465
C5-N1	1.348	1.361	1.361	1.359	1.361	1.361	1.359	1.368	1.368	1.366
C6-N2	1.348	1.361	1.361	1.359	1.361	1.361	1.359	1.368	1.368	1.366

[a] In all cases, the cc-pVDZ basis set was used for C, H, N, and S.

Table S7. Optimised geometry calculated for complex **1** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	78	0.006132	-0.017813	0.006005
2	16	-0.004662	-0.025781	2.265468
3	6	1.688402	-0.050368	2.708821
4	16	2.083445	-0.084353	4.426760
5	6	3.243329	1.327851	4.378998
6	6	4.550208	1.002615	3.686146
7	16	4.387480	0.034343	2.124853
8	6	2.661223	0.081650	1.769217
9	16	2.247320	0.270522	0.076819
10	1	2.718311	2.155784	3.880699
11	1	3.436446	1.617418	5.424118
12	1	5.185534	0.380166	4.333297
13	1	5.090853	1.934770	3.453563
14	7	-0.151818	0.000928	-2.028096
15	6	0.874755	0.106629	-2.895678
16	6	0.695144	0.131833	-4.265621
17	6	-0.600349	0.040930	-4.782957
18	6	-1.659390	-0.074869	-3.899884
19	6	-1.418345	-0.095727	-2.521576
20	6	-2.458671	-0.234380	-1.511056
21	7	-2.008005	-0.246986	-0.225191
22	6	-2.901572	-0.397901	0.772906
23	6	-4.258502	-0.529741	0.546728
24	6	-4.733176	-0.510172	-0.767958
25	6	-3.822136	-0.362653	-1.798991
26	1	1.868128	0.169373	-2.448552
27	1	1.565073	0.221160	-4.916320
28	1	-0.776629	0.057846	-5.859280
29	1	-2.679734	-0.151743	-4.273439
30	1	-4.161879	-0.347911	-2.833834
31	1	-5.798182	-0.611444	-0.980929
32	1	-4.932178	-0.646944	1.395596
33	1	-2.486416	-0.412545	1.781884

Table S8. Optimised geometry calculated for complex **1** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMSO (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	78	0.006685	-0.018752	-0.003146
2	16	0.008325	-0.098195	2.271002
3	6	1.715287	-0.066681	2.702541
4	16	2.119881	-0.130284	4.421059
5	6	3.256442	1.302929	4.420749
6	6	4.565692	1.023696	3.716899
7	16	4.410026	0.128111	2.108989
8	6	2.676208	0.118314	1.764699
9	16	2.255094	0.328750	0.066035
10	1	2.715902	2.139949	3.956395
11	1	3.448885	1.553983	5.474939
12	1	5.210745	0.382247	4.333718
13	1	5.093544	1.970322	3.522345
14	7	-0.156236	0.012894	-2.047745
15	6	0.865148	0.124280	-2.915195
16	6	0.681450	0.124206	-4.288137
17	6	-0.610029	-0.000681	-4.795199
18	6	-1.668055	-0.119481	-3.905459
19	6	-1.419835	-0.109449	-2.532521
20	6	-2.464713	-0.241407	-1.514252
21	7	-2.018383	-0.256410	-0.230826
22	6	-2.910218	-0.389464	0.766571
23	6	-4.271759	-0.505156	0.539487
24	6	-4.740349	-0.482035	-0.772218
25	6	-3.824814	-0.349695	-1.806342
26	1	1.860548	0.211142	-2.478947
27	1	1.547037	0.218000	-4.943288
28	1	-0.791663	-0.008814	-5.870281
29	1	-2.685572	-0.225105	-4.277346
30	1	-4.167015	-0.327501	-2.839485
31	1	-5.805831	-0.565987	-0.988056
32	1	-4.948269	-0.609223	1.387279
33	1	-2.504017	-0.402017	1.778256

Table S9. Optimised geometry calculated for complex **1** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMF (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	1	78	0.006622	-0.019008
2	2	16	0.007828	-0.096462
3	3	6	1.714648	-0.066348
4	4	16	2.119045	-0.128560
5	5	6	3.256467	1.303965
6	6	6	4.565631	1.023210
7	7	16	4.409577	0.124952
8	8	6	2.675891	0.116953
9	9	16	2.255140	0.326769
10	10	1	2.716431	2.140709
11	11	1	3.448934	1.556215
12	12	1	5.210495	0.382507
13	13	1	5.093776	1.969387
14	14	7	-0.156143	0.012430
15	15	6	0.865345	0.123774
16	16	6	0.681733	0.124535
17	17	6	-0.609792	0.000590
18	18	6	-1.667895	-0.118241
19	19	6	-1.419769	-0.109131
20	20	6	-2.464696	-0.241290
21	21	7	-2.018402	-0.256359
22	22	6	-2.910260	-0.389909
23	23	6	-4.271738	-0.505967
24	24	6	-4.740318	-0.482748
25	25	6	-3.824789	-0.349941
26	26	1	1.860734	0.209940
27	27	1	1.547415	0.218291
28	28	1	-0.791356	-0.006776
29	29	1	-2.685456	-0.223098
30	30	1	-4.166948	-0.327765
31	31	1	-5.805770	-0.567054
32	32	1	-4.948237	-0.610458
33	33	1	-2.504002	-0.402626

Table S10. Optimised geometry calculated for complex **2** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	78	-0.019550	-0.000046	0.033888
2	7	-0.031083	0.001823	2.078740
3	6	1.060538	0.007577	2.869110
4	6	0.983460	-0.003243	4.249135
5	6	-0.273990	-0.018336	4.858798
6	6	-1.400361	-0.019132	4.054445
7	6	-1.261657	-0.007200	2.662201
8	6	-2.381525	0.008578	1.728564
9	6	-3.726178	0.013650	2.115393
10	6	-4.719729	0.044321	1.152283
11	6	-4.345868	0.071863	-0.194029
12	6	-3.002196	0.064828	-0.518071
13	7	-2.028701	0.029961	0.413331
14	1	2.020591	0.023177	2.350462
15	1	1.902462	0.000817	4.835344
16	1	-0.370066	-0.027241	5.945332
17	1	-2.393693	-0.027506	4.501368
18	1	-3.987298	-0.005032	3.172741
19	1	-5.771288	0.048886	1.442241
20	1	-5.087585	0.099329	-0.992353
21	1	-2.664293	0.089203	-1.555454
22	16	-0.186956	-0.020728	-2.215842
23	6	1.458954	0.105915	-2.800240
24	16	1.619287	0.273314	-4.551169
25	6	2.490869	-1.265210	-5.011461
26	6	3.999197	-1.264379	-4.807800
27	6	4.470601	-1.293198	-3.360914
28	16	4.200200	0.236830	-2.399417
29	6	2.504065	0.091142	-1.928907
30	16	2.222972	-0.054784	-0.206623
31	1	2.006660	-2.098074	-4.477175
32	1	2.261875	-1.383247	-6.082677
33	1	4.404070	-2.164131	-5.308676
34	1	5.563409	-1.429928	-3.330113
35	1	4.018228	-2.126510	-2.800082
36	1	4.436977	-0.390528	-5.318072

Table S11. Optimised geometry calculated for complex **2** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMSO (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	78	-0.023531	0.011099	0.039037
2	7	-0.033174	-0.002794	2.092862
3	6	1.055281	-0.011110	2.882017
4	6	0.974740	-0.017190	4.264871
5	6	-0.281851	-0.013859	4.866247
6	6	-1.409299	-0.004630	4.057548
7	6	-1.263249	0.001088	2.669881
8	6	-2.388589	0.016802	1.731612
9	6	-3.727328	0.027722	2.124857
10	6	-4.725496	0.048240	1.161291
11	6	-4.359844	0.057444	-0.182918
12	6	-3.014061	0.045848	-0.510858
13	7	-2.042139	0.025289	0.417858
14	1	2.019592	-0.010903	2.373066
15	1	1.891300	-0.023655	4.854066
16	1	-0.383538	-0.017597	5.951854
17	1	-2.401843	-0.000658	4.504436
18	1	-3.988465	0.021425	3.181567
19	1	-5.775073	0.057739	1.456581
20	1	-5.104170	0.074250	-0.978513
21	1	-2.686737	0.055031	-1.550907
22	16	-0.191505	0.015210	-2.225685
23	6	1.466932	0.120389	-2.807223
24	16	1.632145	0.270420	-4.563022
25	6	2.505428	-1.268584	-5.028756
26	6	4.011960	-1.268679	-4.823365
27	6	4.484672	-1.297357	-3.378531
28	16	4.209896	0.232945	-2.413785
29	6	2.510048	0.105222	-1.937511
30	16	2.234247	-0.020028	-0.203178
31	1	2.019287	-2.101758	-4.497698
32	1	2.276236	-1.379537	-6.099887
33	1	4.410953	-2.173090	-5.317678
34	1	5.577488	-1.427531	-3.347417
35	1	4.035395	-2.131067	-2.816736
36	1	4.456695	-0.403375	-5.341683

Table S12. Optimised geometry calculated for complex **2** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMF (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	78	-0.023493	0.010921	0.038973
2	7	-0.033193	-0.002774	2.092763
3	6	1.055299	-0.010904	2.881896
4	6	0.974823	-0.017011	4.264736
5	6	-0.281751	-0.013901	4.866203
6	6	-1.409212	-0.004813	4.057559
7	6	-1.263246	0.000966	2.669851
8	6	-2.388568	0.016701	1.731603
9	6	-3.727361	0.027545	2.124779
10	6	-4.725481	0.048222	1.161199
11	6	-4.359740	0.057674	-0.183008
12	6	-3.013961	0.046119	-0.510889
13	7	-2.042051	0.025372	0.417858
14	1	2.019552	-0.010510	2.372824
15	1	1.891423	-0.023319	4.853879
16	1	-0.383365	-0.017674	5.951824
17	1	-2.401742	-0.000993	4.504497
18	1	-3.988545	0.021058	3.181484
19	1	-5.775082	0.057666	1.456427
20	1	-5.104025	0.074640	-0.978644
21	1	-2.686512	0.055493	-1.550903
22	16	-0.191428	0.014650	-2.225581
23	6	1.466875	0.120190	-2.807189
24	16	1.631958	0.270395	-4.562952
25	6	2.505312	-1.268548	-5.028626
26	6	4.011874	-1.268613	-4.823243
27	6	4.484582	-1.297265	-3.378377
28	16	4.209830	0.232995	-2.413617
29	6	2.509996	0.105064	-1.937473
30	16	2.234105	-0.020487	-0.203261
31	1	2.019227	-2.101732	-4.497523
32	1	2.276146	-1.379608	-6.099762
33	1	4.410919	-2.173009	-5.317586
34	1	5.577402	-1.427508	-3.347287
35	1	4.035279	-2.130981	-2.816605
36	1	4.456559	-0.403259	-5.341530

Table S13. Optimised geometry calculated for complex **3** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	78	0.032207	-0.002622	-0.024622
2	7	0.053757	-0.006433	2.023530
3	6	1.109233	-0.013379	2.844616
4	6	0.978395	-0.029977	4.234639
5	6	-0.280315	-0.035397	4.813942
6	6	-1.410531	-0.021093	3.979648
7	6	-2.764319	-0.016420	4.454377
8	6	-3.816817	0.010242	3.590253
9	6	-3.614230	0.034655	2.170277
10	6	-4.652015	0.075653	1.224306
11	6	-4.328297	0.105014	-0.122618
12	6	-2.990158	0.090769	-0.521344
13	7	-1.980196	0.045159	0.353723
14	6	-2.288755	0.021520	1.684564
15	6	-1.191929	-0.006203	2.585065
16	1	2.089786	-0.003598	2.365224
17	1	1.881030	-0.037560	4.845999
18	1	-0.401682	-0.047599	5.898688
19	1	-2.935251	-0.031815	5.532610
20	1	-4.841205	0.016781	3.967881
21	1	-5.692443	0.086881	1.554364
22	1	-5.103179	0.140348	-0.888691
23	16	-0.167158	-0.024969	-2.272765
24	6	1.478765	0.144684	-2.848024
25	16	1.732625	0.186295	-4.592402
26	6	3.012427	-1.118854	-4.625082
27	6	4.336227	-0.669761	-4.042206
28	16	4.211631	0.311741	-2.485564
29	6	2.531049	0.115564	-1.989126
30	16	2.276197	-0.082403	-0.265144
31	1	2.603192	-1.980729	-4.078180
32	1	3.146923	-1.407938	-5.679497
33	1	4.862635	-0.007556	-4.745273
34	1	4.972450	-1.547457	-3.841725
35	1	-2.710016	0.118213	-1.575925

Table S14. Optimised geometry calculated for complex **3** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMSO (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	78	0.031526	-0.004143	-0.017166
2	7	0.051591	-0.012102	2.042177
3	6	1.102800	-0.021149	2.862199
4	6	0.968493	-0.025674	4.255534
5	6	-0.289515	-0.019538	4.825451
6	6	-1.420233	-0.005693	3.985690
7	6	-2.772307	0.005139	4.462599
8	6	-3.824284	0.024466	3.596875
9	6	-3.616328	0.038041	2.178381
10	6	-4.657743	0.065263	1.230508
11	6	-4.340485	0.083036	-0.113519
12	6	-2.999065	0.073489	-0.513434
13	7	-1.992415	0.043939	0.360190
14	6	-2.294155	0.026131	1.690129
15	6	-1.195524	-0.000052	2.594240
16	1	2.087629	-0.022493	2.393334
17	1	1.868325	-0.033731	4.870038
18	1	-0.415691	-0.023396	5.909222
19	1	-2.942256	-0.001746	5.540433
20	1	-4.849317	0.032597	3.970915
21	1	-5.696961	0.073018	1.562892
22	1	-5.116514	0.105229	-0.878157
23	16	-0.165566	0.018769	-2.281154
24	6	1.497095	0.149140	-2.848536
25	16	1.754833	0.208821	-4.595302
26	6	3.028004	-1.102811	-4.663364
27	6	4.354075	-0.676295	-4.073904
28	16	4.235682	0.248054	-2.479163
29	6	2.544419	0.087378	-1.990181
30	16	2.289083	-0.121041	-0.257861
31	1	2.614205	-1.977435	-4.141638
32	1	3.160178	-1.360481	-5.725209
33	1	4.881749	0.006745	-4.754406
34	1	4.987319	-1.560666	-3.902321
35	1	-2.728616	0.090943	-1.569971

Table S15. Optimised geometry calculated for complex **3** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMF (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	78	0.031543	-0.003836	-0.017397
2	7	0.051639	-0.011815	2.041895
3	6	1.102903	-0.020849	2.861876
4	6	0.968670	-0.025751	4.255199
5	6	-0.289313	-0.019962	4.825227
6	6	-1.420060	-0.006076	3.985544
7	6	-2.772136	0.004531	4.462480
8	6	-3.824142	0.024011	3.596804
9	6	-3.616266	0.037906	2.178292
10	6	-4.657682	0.065384	1.230460
11	6	-4.340410	0.083490	-0.113582
12	6	-2.999015	0.073964	-0.513521
13	7	-1.992332	0.044122	0.360079
14	6	-2.294091	0.026098	1.690007
15	6	-1.195425	-0.000115	2.594070
16	1	2.087671	-0.021867	2.392878
17	1	1.868548	-0.033802	4.869645
18	1	-0.415413	-0.024100	5.909012
19	1	-2.942057	-0.002607	5.540324
20	1	-4.849163	0.032029	3.970902
21	1	-5.696905	0.073093	1.562849
22	1	-5.116447	0.105934	-0.878212
23	16	-0.165670	0.018185	-2.281230
24	6	1.496786	0.149392	-2.848732
25	16	1.754616	0.208405	-4.595477
26	6	3.027801	-1.103265	-4.662669
27	6	4.353852	-0.676477	-4.073251
28	16	4.235180	0.250045	-2.479826
29	6	2.544189	0.088406	-1.990392
30	16	2.288980	-0.119951	-0.258133
31	1	2.613904	-1.977508	-4.140384
32	1	3.160048	-1.361675	-5.724336
33	1	4.881971	0.005598	-4.754396
34	1	4.986748	-1.560876	-3.900447
35	1	-2.728492	0.091696	-1.570037

Table S16. Optimised geometry calculated for complex **4** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	78	0.191712	-0.432150	-0.004737
2	16	0.278436	-0.670458	2.234698
3	6	1.980424	-0.871976	2.600366
4	16	2.340825	-1.237379	4.290485
5	6	3.286317	0.235898	4.814146
6	6	4.760623	0.251162	4.436436
7	6	5.061705	0.438908	2.956233
8	16	4.653507	-0.972668	1.870479
9	6	2.917441	-0.764799	1.619785
10	16	2.445274	-0.422637	-0.032770
11	1	2.758133	1.125513	4.435764
12	1	3.185089	0.233929	5.911253
13	1	4.562467	1.331945	2.547774
14	1	6.145897	0.572815	2.813074
15	7	-0.043127	-0.198471	-2.030774
16	6	0.902564	-0.111113	-2.971480
17	6	0.601553	0.056283	-4.324946
18	6	-0.718456	0.135051	-4.737688
19	6	-1.737121	0.041363	-3.774439
20	6	-3.138729	0.101539	-4.073922
21	6	-4.076803	-0.005631	-3.092248
22	6	-3.701043	-0.183018	-1.719238
23	6	-4.615229	-0.310164	-0.659802
24	6	-4.129200	-0.484266	0.625674
25	6	-2.751913	-0.528742	0.852835
26	7	-1.857049	-0.405778	-0.132555
27	6	-2.326089	-0.237934	-1.404221
28	6	-1.347874	-0.126154	-2.427896
29	1	1.934385	-0.179459	-2.621689
30	1	1.421459	0.121968	-5.040531
31	1	-0.972815	0.265302	-5.791229
32	1	-3.441174	0.233791	-5.114636
33	1	-5.139858	0.039734	-3.336998
34	1	-5.688336	-0.273418	-0.856540
35	1	-4.804670	-0.589438	1.474969
36	1	-2.344297	-0.668488	1.855830
37	1	5.236735	1.087462	4.982610
38	1	5.239167	-0.676205	4.792326

Table S17. Optimised geometry calculated for complex **4** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMSO (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	78	0.184797	-0.422496	-0.010141
2	16	0.272467	-0.680846	2.241407
3	6	1.985738	-0.869405	2.604437
4	16	2.349699	-1.229301	4.298696
5	6	3.310620	0.232084	4.836062
6	6	4.782757	0.238515	4.455939
7	6	5.085348	0.434779	2.978900
8	16	4.660954	-0.965331	1.880104
9	6	2.921251	-0.762613	1.625471
10	16	2.452587	-0.431982	-0.039958
11	1	2.788280	1.128770	4.467767
12	1	3.209682	0.216440	5.932296
13	1	4.595763	1.335204	2.576325
14	1	6.170196	0.554567	2.834273
15	7	-0.049419	-0.181561	-2.045024
16	6	0.893508	-0.082900	-2.982253
17	6	0.590064	0.074912	-4.339612
18	6	-0.728297	0.131533	-4.747379
19	6	-1.747761	0.028839	-3.781020
20	6	-3.148001	0.071358	-4.086453
21	6	-4.086415	-0.035904	-3.104498
22	6	-3.706831	-0.195137	-1.731061
23	6	-4.625115	-0.313935	-0.669768
24	6	-4.146601	-0.466598	0.616807
25	6	-2.766380	-0.501444	0.847417
26	7	-1.873529	-0.390327	-0.136308
27	6	-2.334885	-0.238803	-1.410460
28	6	-1.354444	-0.126645	-2.436381
29	1	1.928313	-0.132744	-2.640742
30	1	1.407793	0.150040	-5.055909
31	1	-0.986105	0.253276	-5.800587
32	1	-3.448102	0.191148	-5.128695
33	1	-5.149500	-0.003313	-3.348357
34	1	-5.697132	-0.285179	-0.870980
35	1	-4.823976	-0.562311	1.464986
36	1	-2.368912	-0.624145	1.855832
37	1	5.259900	1.071993	5.002868
38	1	5.261618	-0.688222	4.812400

Table S18. Optimised geometry calculated for complex **4** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMF (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	78	0.184928	-0.422583	-0.010110
2	16	0.272665	-0.680972	2.241271
3	6	1.985847	-0.869575	2.604316
4	16	2.349764	-1.229735	4.298498
5	6	3.310351	0.231806	4.835935
6	6	4.782519	0.238633	4.455824
7	6	5.085063	0.435071	2.978768
8	16	4.661061	-0.965015	1.879845
9	6	2.921344	-0.762508	1.625358
10	16	2.452558	-0.431519	-0.039880
11	1	2.787825	1.128398	4.467667
12	1	3.209441	0.216146	5.932182
13	1	4.595226	1.335406	2.576288
14	1	6.169890	0.555219	2.834195
15	7	-0.049374	-0.181746	-2.044955
16	6	0.893557	-0.083306	-2.982223
17	6	0.590121	0.074524	-4.339566
18	6	-0.728245	0.131402	-4.747352
19	6	-1.747696	0.028901	-3.780989
20	6	-3.147953	0.071633	-4.086347
21	6	-4.086350	-0.035540	-3.104369
22	6	-3.706774	-0.194918	-1.730938
23	6	-4.625007	-0.313730	-0.669631
24	6	-4.146406	-0.466604	0.616910
25	6	-2.766193	-0.501617	0.847450
26	7	-1.873358	-0.390445	-0.136303
27	6	-2.334804	-0.238748	-1.410405
28	6	-1.354386	-0.126645	-2.436343
29	1	1.928332	-0.133373	-2.640641
30	1	1.407871	0.149458	-5.055869
31	1	-0.986036	0.253169	-5.800569
32	1	-3.448092	0.191500	-5.128578
33	1	-5.149442	-0.002795	-3.348215
34	1	-5.697040	-0.284847	-0.870777
35	1	-4.823738	-0.562362	1.465126
36	1	-2.368602	-0.624490	1.855799
37	1	5.259491	1.072174	5.002846
38	1	5.261570	-0.688052	4.812183

Table S19. Optimised geometry calculated for complex **5** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	6	-0.019368	0.010726	-0.000044
2	6	-0.015427	0.011403	1.399265
3	7	1.150534	-0.001837	2.099590
4	6	2.309117	-0.004818	1.409959
5	6	2.358498	-0.004851	0.031694
6	6	1.169342	0.001288	-0.716854
7	6	-1.219224	0.040790	2.221767
8	7	-0.990616	0.050179	3.562660
9	6	-2.053670	0.100835	4.390586
10	6	-3.354971	0.133348	3.935065
11	6	-3.620196	0.117553	2.555239
12	6	-2.520781	0.071878	1.708979
13	78	0.967813	-0.026331	4.132138
14	16	0.573323	-0.074617	6.358383
15	6	2.162108	0.062567	7.086496
16	6	3.281634	0.037875	6.316828
17	16	4.885645	0.017162	7.049418
18	6	4.503510	-1.262126	8.298182
19	6	3.593396	-0.764393	9.401824
20	16	2.176727	0.273046	8.837445
21	16	3.180595	-0.142551	4.578130
22	6	-5.023732	0.151468	2.035812
23	6	1.196309	0.000508	-2.213572
24	1	4.056262	-2.110161	7.759427
25	1	5.464812	-1.589290	8.725265
26	1	4.148946	-0.119240	10.098355
27	1	3.186334	-1.620895	9.964090
28	1	-1.823223	0.117550	5.457021
29	1	-4.167912	0.172025	4.661924
30	1	-2.673274	0.061801	0.629600
31	1	-0.969423	0.019538	-0.534573
32	1	3.331706	-0.009063	-0.461791
33	1	3.218899	-0.004660	2.012385
34	1	1.734359	0.882362	-2.595381
35	1	1.723608	-0.888170	-2.594581
36	1	0.184060	0.006477	-2.639344
37	1	-5.052474	0.134816	0.938149
38	1	-5.598972	-0.711161	2.407233
39	1	-5.545930	1.058360	2.379032

Table S20. Optimised geometry calculated for complex **5** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMSO (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	6	-0.027427	0.005876	0.000219
2	6	-0.017343	0.020327	1.394584
3	7	1.147430	0.013800	2.090864
4	6	2.303746	0.003574	1.403154
5	6	2.352320	-0.007703	0.022369
6	6	1.164393	-0.010260	-0.720871
7	6	-1.229642	0.046043	2.219217
8	7	-1.010762	0.024179	3.558311
9	6	-2.075018	0.057627	4.380852
10	6	-3.375984	0.110251	3.918522
11	6	-3.629927	0.135766	2.540698
12	6	-2.521543	0.102226	1.697483
13	78	0.957474	-0.027822	4.132857
14	16	0.556029	-0.146230	6.371103
15	6	2.149718	0.019532	7.106726
16	6	3.269232	0.060529	6.343657
17	16	4.874329	0.080973	7.082225
18	6	4.553001	-1.229310	8.317288
19	6	3.625024	-0.786283	9.426407
20	16	2.144148	0.166401	8.868691
21	16	3.187776	-0.058314	4.588200
22	6	-5.025558	0.200658	2.009157
23	6	1.183439	-0.032477	-2.215390
24	1	4.148794	-2.092752	7.769998
25	1	5.528959	-1.510835	8.741171
26	1	4.144582	-0.114308	10.123947
27	1	3.266375	-1.664605	9.985480
28	1	-1.858606	0.045936	5.449413
29	1	-4.192723	0.135171	4.640999
30	1	-2.668325	0.125839	0.618361
31	1	-0.976888	0.003480	-0.533907
32	1	3.324534	-0.016845	-0.471946
33	1	3.218045	0.004733	1.997165
34	1	1.754690	0.823113	-2.606375
35	1	1.682049	-0.944392	-2.578514
36	1	0.170361	0.001089	-2.635181
37	1	-5.042520	0.208648	0.912180
38	1	-5.612325	-0.660846	2.362823
39	1	-5.533514	1.106601	2.373862

Table S21. Optimised geometry calculated for complex **5** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in acetonitrile (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	6	-0.027338	0.006065	0.000123
2	6	-0.017202	0.020175	1.394543
3	7	1.147602	0.013448	2.090758
4	6	2.303890	0.003382	1.402979
5	6	2.352384	-0.007555	0.022204
6	6	1.164417	-0.009867	-0.721000
7	6	-1.229380	0.046016	2.219298
8	7	-1.010255	0.025124	3.558363
9	6	-2.074375	0.058967	4.381078
10	6	-3.375427	0.110862	3.918951
11	6	-3.629653	0.135160	2.541144
12	6	-2.521450	0.101394	1.697770
13	78	0.957966	-0.027529	4.132760
14	16	0.556708	-0.143426	6.370983
15	6	2.150553	0.021355	7.106228
16	6	3.270042	0.059835	6.342961
17	16	4.875145	0.078146	7.081478
18	6	4.551374	-1.230805	8.317315
19	6	3.624127	-0.785486	9.426189
20	16	2.145807	0.170785	8.867926
21	16	3.188113	-0.060847	4.587775
22	6	-5.025463	0.198926	2.009851
23	6	1.183482	-0.031446	-2.215561
24	1	4.145466	-2.093718	7.770445
25	1	5.526801	-1.514041	8.741317
26	1	4.145080	-0.114591	10.123753
27	1	3.263366	-1.662936	9.985308
28	1	-1.857657	0.048193	5.449592
29	1	-4.192048	0.136123	4.641559
30	1	-2.668493	0.124104	0.618655
31	1	-0.976815	0.003905	-0.534001
32	1	3.324573	-0.016544	-0.472178
33	1	3.218160	0.004473	1.997041
34	1	1.753647	0.825032	-2.606226
35	1	1.683133	-0.942588	-2.579191
36	1	0.170365	0.001156	-2.635359
37	1	-5.042623	0.207345	0.912868
38	1	-5.611320	-0.663372	2.363129
39	1	-5.534362	1.104168	2.374973

Table S22. Optimised geometry calculated for complex **5** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in acetone (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	6	-0.027028	0.005949	-0.000003
2	6	-0.016722	0.019347	1.394592
3	7	1.148191	0.011771	2.090618
4	6	2.304368	0.001574	1.402549
5	6	2.352581	-0.008707	0.021831
6	6	1.164469	-0.009858	-0.721270
7	6	-1.228509	0.046053	2.219692
8	7	-1.008644	0.028381	3.558686
9	6	-2.072412	0.063786	4.381873
10	6	-3.373679	0.113667	3.920322
11	6	-3.628750	0.133974	2.542544
12	6	-2.521080	0.099147	1.698760
13	78	0.959506	-0.026498	4.132610
14	16	0.558876	-0.133218	6.370817
15	6	2.153289	0.028235	7.104703
16	6	3.272680	0.058350	6.340741
17	16	4.877697	0.070069	7.079317
18	6	4.546301	-1.235301	8.316978
19	6	3.620916	-0.783548	9.425057
20	16	2.151946	0.186043	8.865482
21	16	3.189154	-0.068951	4.586493
22	6	-5.025086	0.194016	2.011990
23	6	1.183605	-0.028610	-2.215950
24	1	4.135426	-2.096367	7.770907
25	1	5.519961	-1.523924	8.741511
26	1	4.146181	-0.117349	10.123969
27	1	3.252543	-1.658696	9.982921
28	1	-1.854812	0.055809	5.450250
29	1	-4.189949	0.140309	4.643303
30	1	-2.668772	0.118871	0.619647
31	1	-0.976620	0.004626	-0.533999
32	1	3.324668	-0.017846	-0.472781
33	1	3.218568	0.002251	1.996746
34	1	1.739781	0.837929	-2.604894
35	1	1.697540	-0.930690	-2.582027
36	1	0.170041	-0.010530	-2.635625
37	1	-5.042706	0.207342	0.915027
38	1	-5.606726	-0.672945	2.360980
39	1	-5.538455	1.094931	2.381432

Table S23. Optimised geometry calculated for complex **5** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMF (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	6	-0.027355	0.006034	0.000138
2	6	-0.017223	0.020207	1.394550
3	7	1.147572	0.013525	2.090772
4	6	2.303869	0.003427	1.403010
5	6	2.352375	-0.007579	0.022234
6	6	1.164413	-0.009937	-0.720976
7	6	-1.229424	0.046018	2.219287
8	7	-1.010342	0.024963	3.558351
9	6	-2.074480	0.058749	4.381044
10	6	-3.375518	0.110765	3.918882
11	6	-3.629696	0.135259	2.541071
12	6	-2.521466	0.101526	1.697719
13	78	0.957886	-0.027566	4.132780
14	16	0.556593	-0.143910	6.371002
15	6	2.150408	0.021052	7.106319
16	6	3.269902	0.059977	6.343089
17	16	4.875003	0.078648	7.081612
18	6	4.551647	-1.230552	8.317299
19	6	3.624270	-0.785645	9.426218
20	16	2.145514	0.170027	8.868060
21	16	3.188056	-0.060363	4.587853
22	6	-5.025479	0.199218	2.009741
23	6	1.183481	-0.031636	-2.215531
24	1	4.146034	-2.093547	7.770340
25	1	5.527167	-1.513496	8.741275
26	1	4.144982	-0.114579	10.123794
27	1	3.263865	-1.663255	9.985309
28	1	-1.857807	0.047837	5.449564
29	1	-4.192161	0.135978	4.641464
30	1	-2.668471	0.124383	0.618605
31	1	-0.976826	0.003830	-0.533991
32	1	3.324565	-0.016600	-0.472142
33	1	3.218141	0.004533	1.997066
34	1	1.753816	0.824697	-2.606256
35	1	1.682974	-0.942903	-2.579065
36	1	0.170371	0.001107	-2.635331
37	1	-5.042611	0.207548	0.912759
38	1	-5.611496	-0.662935	2.363102
39	1	-5.534209	1.104588	2.374783

Table S24. Optimised geometry calculated for complex **5** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in dichloromethane (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	6	-0.025997	0.006765	-0.000130
2	6	-0.015997	0.018312	1.394882
3	7	1.149151	0.010124	2.090948
4	6	2.305252	0.001026	1.402574
5	6	2.353356	-0.007854	0.021949
6	6	1.165208	-0.007934	-0.721285
7	6	-1.226866	0.045642	2.220459
8	7	-1.005317	0.034832	3.559492
9	6	-2.068331	0.073079	4.383664
10	6	-3.370159	0.118135	3.923479
11	6	-3.627140	0.129884	2.545860
12	6	-2.520692	0.092917	1.701116
13	78	0.962201	-0.023604	4.132389
14	16	0.563066	-0.115319	6.369969
15	6	2.157962	0.040716	7.101459
16	6	3.277037	0.056348	6.336244
17	16	4.881690	0.056211	7.074876
18	6	4.536554	-1.243587	8.314573
19	6	3.614297	-0.781538	9.421586
20	16	2.163323	0.213381	8.860431
21	16	3.190346	-0.082759	4.584198
22	6	-5.024578	0.183347	2.016821
23	6	1.184708	-0.023270	-2.216260
24	1	4.116655	-2.100691	7.769099
25	1	5.506970	-1.542442	8.739782
26	1	4.147328	-0.125082	10.124035
27	1	3.231823	-1.653131	9.975799
28	1	-1.848665	0.071173	5.451707
29	1	-4.185530	0.147317	4.647446
30	1	-2.670234	0.105607	0.622081
31	1	-0.975476	0.006935	-0.534528
32	1	3.325505	-0.016157	-0.472660
33	1	3.219094	0.001980	1.997416
34	1	1.732776	0.849192	-2.603739
35	1	1.706006	-0.919934	-2.585219
36	1	0.171041	-0.012691	-2.636206
37	1	-5.043796	0.190279	0.919713
38	1	-5.604081	-0.683051	2.370849
39	1	-5.540152	1.085234	2.380930

Table S25. Optimised geometry calculated for complex **5** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in chloroform (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	6	-0.024469	0.006830	0.000167
2	6	-0.015262	0.018093	1.395849
3	7	1.149699	0.011857	2.092427
4	6	2.306229	0.005712	1.404085
5	6	2.354568	-0.003144	0.023783
6	6	1.166457	-0.005745	-0.720279
7	6	-1.225396	0.045621	2.221388
8	7	-1.002417	0.042438	3.560321
9	6	-2.065049	0.084628	4.385356
10	6	-3.367045	0.124571	3.926111
11	6	-3.625772	0.126363	2.548339
12	6	-2.520579	0.086599	1.703135
13	78	0.964089	-0.019552	4.133127
14	16	0.565680	-0.103987	6.368667
15	6	2.159868	0.049170	7.099271
16	6	3.278798	0.056545	6.333239
17	16	4.882903	0.049999	7.071856
18	6	4.528976	-1.249425	8.309424
19	6	3.608210	-0.783283	9.416550
20	16	2.169271	0.228970	8.856807
21	16	3.189517	-0.091655	4.583392
22	6	-5.024519	0.172128	2.021077
23	6	1.187453	-0.022084	-2.215568
24	1	4.103158	-2.102327	7.761868
25	1	5.497067	-1.556306	8.734632
26	1	4.146238	-0.134505	10.122567
27	1	3.216838	-1.653745	9.966727
28	1	-1.843025	0.090144	5.453005
29	1	-4.181902	0.157272	4.650629
30	1	-2.671230	0.091628	0.624074
31	1	-0.973906	0.006434	-0.534549
32	1	3.326892	-0.008828	-0.470703
33	1	3.219221	0.009605	2.000397
34	1	1.746985	0.842532	-2.604229
35	1	1.696347	-0.926276	-2.583912
36	1	0.174434	0.001173	-2.636918
37	1	-5.045443	0.179011	0.923855
38	1	-5.598975	-0.697959	2.374623
39	1	-5.545570	1.070888	2.385206

Table S26. Optimised geometry calculated for complex **5** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in THF (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	6	-0.025702	0.006986	-0.000114
2	6	-0.015805	0.018747	1.395085
3	7	1.149208	0.011789	2.091204
4	6	2.305481	0.004377	1.402874
5	6	2.353600	-0.004575	0.022361
6	6	1.165420	-0.006545	-0.721082
7	6	-1.226593	0.046025	2.220699
8	7	-1.004726	0.037895	3.559600
9	6	-2.067645	0.077468	4.384027
10	6	-3.369484	0.120493	3.924011
11	6	-3.626892	0.128721	2.546297
12	6	-2.520757	0.091018	1.701484
13	78	0.962676	-0.022069	4.132637
14	16	0.563688	-0.113218	6.369631
15	6	2.158468	0.041915	7.101012
16	6	3.277457	0.055536	6.335578
17	16	4.882076	0.053713	7.073972
18	6	4.534761	-1.245710	8.313476
19	6	3.613312	-0.781983	9.420566
20	16	2.164375	0.215818	8.859655
21	16	3.189989	-0.085766	4.583992
22	6	-5.024728	0.179129	2.017778
23	6	1.185434	-0.023681	-2.216111
24	1	4.113019	-2.101763	7.767755
25	1	5.504604	-1.546695	8.738581
26	1	4.147773	-0.126511	10.122909
27	1	3.229319	-1.652907	9.974890
28	1	-1.847320	0.078412	5.451958
29	1	-4.184822	0.150809	4.648004
30	1	-2.670475	0.101244	0.622417
31	1	-0.975230	0.006363	-0.534485
32	1	3.325754	-0.011223	-0.472319
33	1	3.219064	0.007032	1.998148
34	1	1.747723	0.839010	-2.604876
35	1	1.692071	-0.929468	-2.583520
36	1	0.172268	0.002114	-2.636676
37	1	-5.044407	0.187160	0.920656
38	1	-5.601768	-0.689382	2.370770
39	1	-5.542848	1.079114	2.382957

Table S27. Optimised geometry calculated for complex **5** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in toluene (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z
1	6	-0.022222	0.007008	0.000724
2	6	-0.014755	0.016191	1.397540
3	7	1.150259	0.009819	2.095361
4	6	2.307442	0.005398	1.406817
5	6	2.356257	-0.002417	0.027083
6	6	1.168137	-0.004329	-0.718491
7	6	-1.223150	0.044346	2.222390
8	7	-0.998047	0.049231	3.561673
9	6	-2.060508	0.096324	4.387740
10	6	-3.362527	0.131628	3.929859
11	6	-3.623730	0.122599	2.551747
12	6	-2.520480	0.078892	1.706051
13	78	0.966054	-0.017650	4.133782
14	16	0.568858	-0.089125	6.365907
15	6	2.161465	0.059023	7.095324
16	6	3.280383	0.054953	6.328058
17	16	4.883962	0.041895	7.065703
18	6	4.519130	-1.255226	8.302207
19	6	3.600309	-0.782644	9.409044
20	16	2.175416	0.248861	8.850690
21	16	3.187022	-0.106370	4.581972
22	6	-5.024232	0.161451	2.027059
23	6	1.191245	-0.017289	-2.214323
24	1	4.086129	-2.103968	7.753591
25	1	5.484395	-1.571285	8.727767
26	1	4.144548	-0.141983	10.118063
27	1	3.198836	-1.650949	9.955981
28	1	-1.835217	0.109189	5.454859
29	1	-4.176548	0.168505	4.655300
30	1	-2.672399	0.074646	0.626969
31	1	-0.971638	0.008564	-0.534389
32	1	3.328966	-0.006994	-0.466930
33	1	3.219202	0.010365	2.005377
34	1	1.740994	0.854336	-2.601824
35	1	1.708865	-0.915315	-2.585825
36	1	0.178428	-0.003240	-2.637235
37	1	-5.047872	0.159476	0.929609
38	1	-5.597412	-0.706924	2.387221
39	1	-5.547222	1.062397	2.383348

Table S28. Optimised geometry calculated for complex **6** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in the gas phase (total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z	Atom number	*Z*	x	y	z
1	6	-3.175848	-1.512666	0.029628	30	1	-4.128510	1.023090	0.072988
2	6	-2.016970	-0.736016	0.009422	31	1	-4.141272	-1.009075	0.065302
3	7	-0.783369	-1.311896	-0.032687	32	1	-1.683112	-4.543703	-0.075703
4	6	-0.715222	-2.653780	-0.065449	33	1	0.289574	-3.077118	-0.109614
5	6	-1.834600	-3.466069	-0.048170	34	6	-4.103925	-5.238170	-0.009600
6	6	-3.119101	-2.905286	0.002723	35	6	-5.181175	-3.421950	1.310083
7	6	-2.005950	0.724414	0.015547	36	6	-5.253860	-3.378119	-1.200780
8	7	-0.767295	1.280892	-0.021202	37	6	-5.613125	3.020171	0.104938
9	6	-0.679243	2.625783	-0.041636	38	6	-4.231110	4.711279	1.302435
10	6	-1.785566	3.448095	-0.016936	39	6	-4.308475	4.686486	-1.208587
11	6	-3.082571	2.903740	0.028396	40	1	-6.109748	-4.013334	1.341972
12	6	-3.159602	1.516408	0.042352	41	1	-4.588772	-3.667072	2.204909
13	78	0.800653	-0.024866	-0.029468	42	1	-5.461490	-2.359512	1.371815
14	16	2.427842	1.546378	0.002524	43	1	-5.049506	-5.800341	0.008622
15	6	3.913585	0.638473	-0.207070	44	1	-3.564471	-5.529737	-0.923751
16	6	3.901123	-0.719843	-0.215585	45	1	-3.511560	-5.560419	0.860438
17	16	5.405316	-1.639383	-0.266237	46	1	-6.182810	-3.969783	-1.200180
18	6	6.266215	-0.658291	1.013855	47	1	-5.537126	-2.314686	-1.208474
19	6	6.656582	0.726852	0.541076	48	1	-4.714002	-3.590199	-2.136354
20	16	5.368038	1.608519	-0.440873	49	1	-5.101603	5.385138	1.335316
21	16	2.409182	-1.613506	-0.006200	50	1	-4.228348	4.110177	2.224706
22	6	-4.306752	3.814076	0.056798	51	1	-3.325829	5.336349	1.304886
23	6	-4.399556	-3.737541	0.025094	52	1	-6.466156	3.714625	0.124995
24	1	5.595524	-0.611996	1.884187	53	1	-5.735286	2.375549	-0.779426
25	1	7.167417	-1.224200	1.298797	54	1	-5.679530	2.392227	1.007069
26	1	7.527276	0.674619	-0.129195	55	1	-5.180255	5.359450	-1.201510
27	1	6.916992	1.356853	1.407550	56	1	-3.405915	5.311554	-1.278653
28	1	0.331749	3.034213	-0.082044	57	1	-4.361194	4.067336	-2.117305
29	1	-1.623518	4.526159	-0.034270					

Table S29. Optimised geometry calculated for complex **6** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMSO (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z	Atom number	*Z*	x	y	z
1	6	-3.178422	-1.510866	0.041001	30	1	1	-4.134175	1.011571
2	6	-2.020451	-0.741417	0.003173	31	1	1	-4.142054	-1.007000
3	7	-0.791131	-1.319246	-0.052633	32	1	1	-1.694208	-4.548738
4	6	-0.722792	-2.658390	-0.083197	33	1	1	0.277043	-3.090462
5	6	-1.844461	-3.471198	-0.052443	34	6	6	-4.113776	-5.235650
6	6	-3.122833	-2.907831	0.015750	35	6	6	-5.163902	-3.401663
7	6	-2.011224	0.725900	0.017471	36	6	6	-5.270498	-3.374056
8	7	-0.777745	1.288004	0.013488	37	6	6	-5.625861	2.994509
9	6	-0.692573	2.630574	0.014570	38	6	6	-4.285706	4.698963
10	6	-1.803920	3.450405	0.021090	39	6	6	-4.293660	4.668084
11	6	-3.094726	2.899378	0.021756	40	1	1	-6.093846	-3.989235
12	6	-3.166875	1.507694	0.020293	41	1	1	-4.560590	-3.647239
13	78	0.797297	-0.023285	-0.029732	42	1	1	-5.438537	-2.337729
14	16	2.434123	1.556334	0.079579	43	1	1	-5.063031	-5.790198
15	6	3.926828	0.650491	-0.165550	44	1	1	-3.588864	-5.535637
16	6	3.916362	-0.702296	-0.250762	45	1	1	-3.511280	-5.553634
17	16	5.423481	-1.618965	-0.354688	46	1	1	-6.202025	-3.960481
18	6	6.311474	-0.710230	0.961162	47	1	1	-5.546515	-2.308961
19	6	6.698471	0.694983	0.556697	48	1	1	-4.745057	-3.600580
20	16	5.381835	1.641825	-0.327410	49	1	1	-5.164183	5.362488
21	16	2.419133	-1.619279	-0.108618	50	1	1	-4.303826	4.098758
22	6	-4.325539	3.799120	0.016808	51	1	1	-3.387517	5.333832
23	6	-4.403952	-3.734289	0.061379	52	1	1	-6.481508	3.685614
24	1	5.660329	-0.713111	1.846831	53	1	1	-5.720608	2.349948
25	1	7.216809	-1.291977	1.192160	54	1	1	-5.710482	2.365488
26	1	7.548082	0.679912	-0.140446	55	1	1	-5.171015	5.333000
27	1	6.985624	1.273653	1.448489	56	1	1	-3.393973	5.299734
28	1	0.313636	3.050174	0.004631	57	1	1	-4.319546	4.045131
29	1	-1.644705	4.528658	0.021205					

Table S30. Optimised geometry calculated for complex **6** at DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMF (SCRF IEF-PCM; total charge = 0, spin multiplicity = 1) in orthogonal Cartesian coordinate format (*Z* = atomic number).

Atom number	*Z*	x	y	z	Atom number	*Z*	x	y	z
1	6	-3.178359	-1.510952	0.041224	30	1	-4.134153	1.011698	0.015003
2	6	-2.020421	-0.741410	0.003205	31	1	-4.142044	-1.007209	0.096234
3	7	-0.791075	-1.319193	-0.052926	32	1	-1.694081	-4.548707	-0.080936
4	6	-0.722722	-2.658326	-0.083933	33	1	0.277152	-3.090275	-0.134986
5	6	-1.844356	-3.471177	-0.053178	34	6	-4.113672	-5.235740	0.031949
6	6	-3.122740	-2.907885	0.015567	35	6	-5.163036	-3.402622	1.356216
7	6	-2.011188	0.725882	0.017399	36	6	-5.271139	-3.373422	-1.155472
8	7	-0.777670	1.287930	0.012893	37	6	-5.625768	2.994823	0.031762
9	6	-0.692459	2.630498	0.013585	38	6	-4.285008	4.698987	1.263020
10	6	-1.803766	3.450372	0.020374	39	6	-4.293932	4.668435	-1.250542
11	6	-3.094616	2.899430	0.021701	40	1	-6.093043	-3.990086	1.401035
12	6	-3.166817	1.507767	0.020458	41	1	-4.559245	-3.648822	2.243171
13	78	0.797326	-0.023308	-0.029872	42	1	-5.437466	-2.338677	1.413689
14	16	2.434028	1.556274	0.079056	43	1	-5.062875	-5.790374	0.067544
15	6	3.926668	0.650442	-0.165825	44	1	-3.589237	-5.535104	-0.888349
16	6	3.916213	-0.702381	-0.250542	45	1	-3.510713	-5.554296	0.896024
17	16	5.423385	-1.618937	-0.354146	46	1	-6.202641	-3.959887	-1.133408
18	6	6.310820	-0.709967	0.961907	47	1	-5.547223	-2.308329	-1.164900
19	6	6.697769	0.695316	0.557497	48	1	-4.746254	-3.599228	-2.096415
20	16	5.381753	1.641497	-0.328189	49	1	-5.163397	5.362629	1.269008
21	16	2.419099	-1.619251	-0.107642	50	1	-4.302793	4.098698	2.185645
22	6	-4.325364	3.799295	0.017256	51	1	-3.386734	5.333743	1.284719
23	6	-4.403840	-3.734396	0.061355	52	1	-6.481384	3.685967	0.030374
24	1	5.659286	-0.712796	1.847292	53	1	-5.720867	2.350316	-0.855642
25	1	7.216121	-1.291604	1.193387	54	1	-5.710167	2.365797	0.931313
26	1	7.548027	0.680325	-0.138877	55	1	-5.171251	5.333410	-1.265833
27	1	6.983971	1.274227	1.449459	56	1	-3.394238	5.300053	-1.294810
28	1	0.313798	3.049983	0.003100	57	1	-4.320107	4.045645	-2.157942
29	1	-1.644494	4.528622	0.020174					

Table S31. Selected optimised bond lengths (Å) and angles (°) calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] in the gas phase for complexes **1**–**6**; numbering scheme as in Figure S5.

1		**2**		**3**		**4**		**5**		**6**	
Pt-S1	2.261	Pt-S1	2.256	Pt-S1	2.258	Pt-S1	2.254	Pt-S1	2.261	Pt-S1	2.262
Pt-S2	2.260	Pt-S2	2.256	Pt-S2	2.258	Pt-S2	2.254	Pt-S2	2.260	Pt-S2	2.261
Pt-N1	2.040	Pt-N1	2.045	Pt-N1	2.048	Pt-N1	2.053	Pt-N1	2.041	Pt-N1	2.041
Pt-N2	2.040	Pt-N2	2.045	Pt-N2	2.048	Pt-N2	2.053	Pt-N2	2.041	Pt-N2	2.041
S1-C11	1.752	S1-C11	1.751	S1-C13	1.754	S1-C13	1.752	S1-C13	1.753	S1-C13	1.754
S2-C12	1.750	S2-C12	1.751	S2-C14	1.752	S2-C14	1.752	S2-C14	1.751	S2-C14	1.752
C11-S3	1.763	C11-S3	1.766	C13-S3	1.763	C13-S3	1.760	C13-S3	1.764	C13-S3	1.764
C12-S4	1.763	C12-S4	1.766	C14-S4	1.763	C14-S4	1.766	C14-S4	1.763	C14-S4	1.764
S3-C13	1.844	S3-C13	1.827	S3-C15	1.844	S3-C15	1.827	S3-C15	1.844	S3-C15	1.844
S4-C14	1.828	S4-C15	1.827	S4-C16	1.828	S4-C17	1.827	S4-C16	1.828	S4-C16	1.828
C11-C12	1.359	C11-C12	1.361	C13-C14	1.359	C13-C14	1.361	C13-C14	1.359	C13-C14	1.358
C13-C14	1.515	C13-C14	1.522	C15-C16	1.515	C15-C16	1.522	C15-C16	1.515	C15-C16	1.515
		C14-C15	1.522			C16-C17	1.522				
N1-C5	1.363	N1-C5	1.362	N1-C6	1.366	N1-C6	1.366	N1-C6	1.360	N1-C6	1.358
N2-C6	1.363	N2-C6	1.362	N2-C7	1.366	N2-C7	1.366	N2-C7	1.360	N2-C7	1.362
C5-C6	1.457	C5-C6	1.458	C6-C7	1.419	C6-C7	1.420	C6-C7	1.458	C6-C7	1.460
N1-Pt-S1	96.13	N1-Pt-S1	96.44	N1-Pt-S1	95.51	N1-Pt-S1	95.83	N1-Pt-S1	96.20	N1-Pt-S1	96.21
S1-Pt-S2	88.50	S1-Pt-S2	88.12	S1-Pt-S2	88.93	S1-Pt-S2	88.53	S1-Pt-S2	88.59	S1-Pt-S2	88.64
S2-Pt-N2	96.21	S2-Pt-N2	96.44	S2-Pt-N2	95.59	S2-Pt-N2	95.83	S2-Pt-N2	96.29	S2-Pt-N2	96.27
N1-Pt-N2	79.14	N1-Pt-N2	78.90	N1-Pt-N2	79.96	N1-Pt-N2	79.80	N1-Pt-N2	78.91	N1-Pt-N2	78.88
N1-Pt-S1-C11	172.96	N1-Pt-S1-C11	174.76	N1-Pt-S1-C13	173.10	N1-Pt-S1-C13	174.87	N1-Pt-S1-C13	173.02	N1-Pt-S1-C13	173.03
N2-Pt-S2-C12	172.71	N2-Pt-S2-C12	174.77	N2-Pt-S2-C14	172.84	N2-Pt-S2-C14	174.88	N2-Pt-S2-C14	172.76	N2-Pt-S2-C14	172.74
Pt-S1-C11-S3	172.00	Pt-S1-C11-S3	174.25	Pt-S1-C13-S3	172.23	Pt-S1-C13-S3	174.43	Pt-S1-C13-S3	172.11	Pt-S1-C13-S3	172.19
Pt-S2-C12-S4	179.18	Pt-S2-C12-S4	174.25	Pt-S2-C14-S4	179.39	Pt-S2-C14-S4	174.43	Pt-S2-C14-S4	179.30	Pt-S2-C14-S4	179.38
S1-C11-S3-C13	140.64	S1-C11-S3-C13	115.51	S1-C13-S3-C15	140.38	S1-C13-S3-C15	115.39	S1-C13-S3-C15	140.38	S1-C13-S3-C15	140.04
S2-C12-S4-C14	128.53	S2-C12-S4-C15	115.51	S2-C14-S4-C16	128.37	S2-C14-S4-C17	115.39	S2-C14-S4-C16	128.35	S2-C14-S4-C16	128.11
		C11-S3-C13-C14	81.08			C13-S3-C15-C16	81.14				
		C12-S4-C15-C14	81.07			C14-S4-C17-C16	81.14				

Table S32. Selected optimised bond lengths (Å) and angles (°) calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMSO (SCRF IEF-PCM) for complexes **1**–**6**; numbering scheme as in Figure S5.

1		**2**		**3**		**4**		**5**		**6**	
Pt-S1	2.271	Pt-S1	2.271	Pt-S1	2.273	Pt-S1	2.268	Pt-S1	2.277	Pt-S1	2.277
Pt-S2	2.271	Pt-S2	2.271	Pt-S2	2.273	Pt-S2	2.268	Pt-S2	2.277	Pt-S2	2.277
Pt-N1	2.054	Pt-N1	2.054	Pt-N1	2.059	Pt-N1	2.062	Pt-N1	2.051	Pt-N1	2.050
Pt-N2	2.054	Pt-N2	2.054	Pt-N2	2.059	Pt-N2	2.062	Pt-N2	2.051	Pt-N2	2.050
S1-C11	1.761	S1-C11	1.761	S1-C13	1.763	S1-C13	1.761	S1-C13	1.763	S1-C13	1.763
S2-C12	1.761	S2-C12	1.761	S2-C14	1.762	S2-C14	1.761	S2-C14	1.761	S2-C14	1.762
C11-S3	1.770	C11-S3	1.770	C13-S3	1.768	C13-S3	1.770	C13-S3	1.768	C13-S3	1.768
C12-S4	1.770	C12-S4	1.770	C14-S4	1.767	C14-S4	1.770	C14-S4	1.768	C14-S4	1.767
S3-C13	1.830	S3-C13	1.830	S3-C15	1.847	S3-C15	1.830	S3-C15	1.847	S3-C15	1.847
S4-C14	1.830	S4-C15	1.830	S4-C16	1.829	S4-C17	1.830	S4-C16	1.829	S4-C16	1.829
C11-C12	1.358	C11-C12	1.358	C13-C14	1.356	C13-C14	1.358	C13-C14	1.355	C13-C14	1.356
C13-C14	1.521	C13-C14	1.520	C15-C16	1.513	C15-C16	1.520	C15-C16	1.513	C15-C16	1.513
		C14-C15	1.521			C16-C17	1.520				
N1-C5	1.359	N1-C5	1.359	N1-C6	1.364	N1-C6	1.364	N1-C6	1.357	N1-C6	1.356
N2-C6	1.359	N2-C6	1.359	N2-C7	1.364	N2-C7	1.364	N2-C7	1.357	N2-C7	1.360
C5-C6	1.465	C5-C6	1.465	C6-C7	1.423	C6-C7	1.424	C6-C7	1.466	C6-C7	1.467
N1-Pt-S1	96.38	N1-Pt-S1	96.38	N1-Pt-S1	95.51	N1-Pt-S1	95.80	N1-Pt-S1	93.17	N1-Pt-S1	96.17
S1-Pt-S2	88.12	S1-Pt-S2	88.12	S1-Pt-S2	88.92	S1-Pt-S2	88.51	S1-Pt-S2	88.59	S1-Pt-S2	88.62
S2-Pt-N2	96.39	S2-Pt-N2	96.39	S2-Pt-N2	95.57	S2-Pt-N2	95.80	S2-Pt-N2	96.24	S2-Pt-N2	96.22
N1-Pt-N2	79.21	N1-Pt-N2	79.11	N1-Pt-N2	80.00	N1-Pt-N2	79.59	N1-Pt-N2	79.02	N1-Pt-N2	79.01
N1-Pt-S1-C11	172.40	N1-Pt-S1-C11	176.04	N1-Pt-S1-C13	172.76	N1-Pt-S1-C13	175.59	N1-Pt-S1-C13	175.52	N1-Pt-S1-C13	172.55
N2-Pt-S2-C12	174.20	N2-Pt-S2-C12	176.07	N2-Pt-S2-C14	174.37	N2-Pt-S2-C14	175.57	N2-Pt-S2-C14	174.73	N2-Pt-S2-C14	174.86
Pt-S1-C11-S3	172.64	Pt-S1-C11-S3	175.41	Pt-S1-C13-S3	172.62	Pt-S1-C13-S3	175.06	Pt-S1-C13-S3	172.77	Pt-S1-C13-S3	172.99
Pt-S2-C12-S4	179.47	Pt-S2-C12-S4	175.41	Pt-S2-C14-S4	179.56	Pt-S2-C14-S4	175.06	Pt-S2-C14-S4	179.49	Pt-S2-C14-S4	179.49
S1-C11-S3-C13	142.28	S1-C11-S3-C13	116.08	S1-C13-S3-C15	141.90	S1-C13-S3-C15	116.23	S1-C13-S3-C15	142.38	S1-C13-S3-C15	142.18
S2-C12-S4-C14	129.73	S2-C12-S4-C15	116.07	S2-C14-S4-C16	129.66	S2-C14-S4-C17	116.23	S2-C14-S4-C16	129.73	S2-C14-S4-C16	129.46
		C11-S3-C13-C14	80.76			C13-S3-C15-C16	80.77				
		C12-S4-C15-C14	80.76			C14-S4-C17-C16	80.76				

Table S33. Selected optimised bond lengths (Å) and angles (°) calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMF (SCRF IEF-PCM) for complexes **1**–**6**; numbering scheme as in Figure S5.

1		**2**		**3**		**4**		**5**		**6**	
Pt-S1	2.276	Pt-S1	2.271	Pt-S1	2.273	Pt-S1	2.268	Pt-S1	2.277	Pt-S1	2.277
Pt-S2	2.276	Pt-S2	2.271	Pt-S2	2.272	Pt-S2	2.268	Pt-S2	2.276	Pt-S2	2.277
Pt-N1	2.051	Pt-N1	2.054	Pt-N1	2.059	Pt-N1	2.062	Pt-N1	2.051	Pt-N1	2.050
Pt-N2	2.051	Pt-N2	2.054	Pt-N2	2.059	Pt-N2	2.062	Pt-N2	2.051	Pt-N2	2.050
S1-C11	1.763	S1-C11	1.760	S1-C13	1.763	S1-C13	1.761	S1-C13	1.763	S1-C13	1.763
S2-C12	1.761	S2-C12	1.760	S2-C14	1.761	S2-C14	1.761	S2-C14	1.761	S2-C14	1.761
C11-S3	1.768	C11-S3	1.770	C13-S3	1.768	C13-S3	1.770	C13-S3	1.768	C13-S3	1.768
C12-S4	1.767	C12-S4	1.770	C14-S4	1.767	C14-S4	1.770	C14-S4	1.767	C14-S4	1.767
S3-C13	1.847	S3-C13	1.830	S3-C15	1.847	S3-C15	1.830	S3-C15	1.847	S3-C15	1.847
S4-C14	1.829	S4-C15	1.830	S4-C16	1.829	S4-C17	1.830	S4-C16	1.829	S4-C16	1.826
C11-C12	1.355	C11-C12	1.358	C13-C14	1.356	C13-C14	1.358	C13-C14	1.355	C13-C14	1.355
C13-C14	1.513	C13-C14	1.520	C15-C16	1.513	C15-C16	1.520	C15-C16	1.513	C15-C16	1.513
		C14-C15	1.521			C16-C17	1.520				
N1-C5	1.359	N1-C5	1.359	N1-C6	1.364	N1-C6	1.364	N1-C6	1.357	N1-C6	1.356
N2-C6	1.359	N2-C6	1.359	N2-C7	1.364	N2-C7	1.364	N2-C7	1.357	N2-C7	1.359
C5-C6	1.465	C5-C6	1.465	C6-C7	1.423	C6-C7	1.423	C6-C7	1.466	C6-C7	1.467
N1-Pt-S1	96.11	N1-Pt-S1	96.39	N1-Pt-S1	95.510	N1-Pt-S1	95.80	N1-Pt-S1	96.170	N1-Pt-S1	96.17
S1-Pt-S2	88.53	S1-Pt-S2	88.12	S1-Pt-S2	88.92	S1-Pt-S2	88.50	S1-Pt-S2	88.590	S1-Pt-S2	88.62
S2-Pt-N2	96.18	S2-Pt-N2	96.39	S2-Pt-N2	95.57	S2-Pt-N2	95.80	S2-Pt-N2	96.240	S2-Pt-N2	96.22
N1-Pt-N2	79.21	N1-Pt-N2	79.10	N1-Pt-N2	80.00	N1-Pt-N2	79.89	N1-Pt-N2	79.010	N1-Pt-N2	79.00
N1-Pt-S1-C11	172.43	N1-Pt-S1-C11	176.02	N1-Pt-S1-C13	172.76	N1-Pt-S1-C13	175.57	N1-Pt-S1-C13	172.550	N1-Pt-S1-C13	172.550
N2-Pt-S2-C12	174.60	N2-Pt-S2-C12	176.05	N2-Pt-S2-C14	174.34	N2-Pt-S2-C14	175.57	N2-Pt-S2-C14	174.69	N2-Pt-S2-C14	174.83
Pt-S1-C11-S3	172.62	Pt-S1-C11-S3	175.40	Pt-S1-C13-S3	172.60	Pt-S1-C13-S3	175.06	Pt-S1-C13-S3	172.75	Pt-S1-C13-S3	172.98
Pt-S2-C12-S4	179.48	Pt-S2-C12-S4	175.39	Pt-S2-C14-S4	179.57	Pt-S2-C14-S4	175.06	Pt-S2-C14-S4	179.51	Pt-S2-C14-S4	179.47
S1-C11-S3-C13	142.23	S1-C11-S3-C13	116.07	S1-C13-S3-C15	141.91	S1-C13-S3-C15	116.23	S1-C13-S3-C15	142.30	S1-C13-S3-C15	142.14
S2-C12-S4-C14	129.70	S2-C12-S4-C15	116.06	S2-C14-S4-C16	129.63	S2-C14-S4-C17	116.22	S2-C14-S4-C16	129.70	S2-C14-S4-C16	129.43
		C11-S3-C13-C14	80.76			C13-S3-C15-C16	80.76				
		C12-S4-C15-C14	80.77			C14-S4-C17-C16	80.77				

Table S34. Selected optimised bond lengths (Å) and angles (°) calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] in different solvents (SCRF IEF-PCM) for complex **5**; numbering scheme as in Figure S5.

	CH_3CN	DMSO	Acetone	DMF	DCM	$CHCl_3$	THF	Toluene
Pt-S1	2.277	2.277	2.276	2.277	2.275	2.272	2.274	2.268
Pt-S2	2.276	2.277	2.276	2.276	2.274	2.272	2.274	2.267
Pt-N1	2.051	2.051	2.051	2.051	2.050	2.049	2.050	2.047
Pt-N2	2.051	2.051	2.051	2.051	2.050	2.049	2.050	2.047
S1-C11	1.763	1.763	1.763	1.763	1.762	1.760	1.761	1.785
S2-C12	1.761	1.761	1.761	1.761	1.760	1.758	1.759	1.756
C11-S3	1.768	1.768	1.768	1.768	1.767	1.767	1.767	1.766
C12-S4	1.767	1.768	1.767	1.767	1.766	1.766	1.766	1.765
S3-C13	1.847	1.847	1.847	1.847	1.847	1.846	1.847	1.845
S4-C14	1.829	1.829	1.829	1.829	1.829	1.829	1.829	1.829
C11-C12	1.355	1.355	1.356	1.355	1.356	1.356	1.356	1.357
C13-C14	1.513	1.513	1.513	1.513	1.513	1.514	1.513	1.514
N1-C5	1.357	1.357	1.357	1.357	1.357	1.357	1.357	1.358
N2-C6	1.357	1.357	1.357	1.357	1.357	1.357	1.357	1.358
C5-C6	1.466	1.466	1.466	1.466	1.466	1.465	1.466	1.463
N1-Pt-S1	96.17	93.17	96.17	96.17	96.18	96.19	96.18	96.20
S1-Pt-S2	88.59	88.59	88.59	88.59	88.59	88.60	88.59	88.61
S2-Pt-N2	96.24	96.24	96.24	96.24	96.25	96.27	96.26	96.27
N1-Pt-N2	79.01	79.02	79.00	79.01	78.98	78.94	78.96	78.90
N1-Pt-S1-C11	172.55	175.52	172.63	172.55	172.77	172.79	172.76	172.86
N2-Pt-S2-C12	174.68	174.73	174.50	174.69	174.16	173.87	174.07	173.46
Pt-S1-C11-S3	172.74	172.77	172.66	172.75	172.49	172.41	172.46	172.35
Pt-S2-C12-S4	179.51	179.49	179.57	179.51	179.68	179.66	179.64	179.58
S1-C11-S3-C13	142.28	142.38	141.93	142.30	141.20	140.66	141.13	140.14
S2-C12-S4-C14	129.70	129.73	129.55	129.70	129.23	128.85	129.15	128.39

Table S35. Frontier molecular orbital composition (%) calculated calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] at the optimised geometry in the gas phase for complexes **1**–**6** in terms of diimine N^N, 1,2-dithiolene ligand S^S, and platinum atom.

		N^N	S^S	Pt
1	HOMO	12	82	6
	LUMO	85	10	5
2	HOMO	13	79	8
	LUMO	86	9	5
3	HOMO	12	82	6
	LUMO	86	9	5
4	HOMO	13	79	8
	LUMO	86	9	5
5	HOMO	12	82	6
	LUMO	86	9	5
6	HOMO	12	82	6
	LUMO	87	8	5

Table S36. Selected natural charges on the diimine N^N, 1,2-dithiolene ligand S^S, and platinum atom (|*e*|) calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] at the optimised geometry in the gas phase for complexes **1**–**6**.

	N^N	S^S	Pt
1	0.285	–0.319	0.034
2	0.307	–0.338	0.031
3	0.322	–0.351	0.029
4	0.289	–0.310	0.022
5	0.292	–0.321	0.029
6	0.295	–0.312	0.017

Table S37. Eigenvalues of Kohn-Sham HOMO and LUMO and HOMO-LUMO energy gap (eV) calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] in the gas phase, DMSO, and DMF (SCRF IEF-PCM) for complexes **1**–**6**.

	Gas			DMSO			DMF		
	HOMO	LUMO	$\Delta E_{\text{HOMO-LUMO}}$	HOMO	LUMO	$\Delta E_{\text{HOMO-LUMO}}$	HOMO	LUMO	$\Delta E_{\text{HOMO-LUMO}}$
1	–4.534	–2.629	1.905	–5.123	–2.521	2.602	–5.114	–2.521	2.593
2	–4.670	–2.622	2.048	–5.251	–2.509	2.742	–5.242	–2.510	2.732
3	–4.505	–2.592	1.913	–5.118	–2.496	2.620	–5.110	–2.496	2.614
4	–4.639	–2.585	2.054	–5.242	–2.484	2.758	–5.234	–2.484	2.750
5	–4.410	–2.497	1.913	–5.086	–2.434	2.652	–5.077	–2.434	2.643
6	–4.351	–2.391	1.960	–5.086	–2.390	2.696	–5.234	–2.484	2.750

Table S38. Eigenvalues of Kohn-Sham HOMO and LUMO and HOMO-LUMO energy gap (eV) calculated at the DFT level level [PBE0//cc-pVDZ/LANL08(f)] in different solvents (SCRF IEF-PCM) for complex **5**.

	HOMO	LUMO	$\Delta E_{\text{HOMO-LUMO}}$
CH_3CN	–5.075	–2.434	2.641
DMSO	–5.086	–2.434	2.652
Acetone	–5.044	–2.434	2.610
DMF	–5.077	–2.434	2.643
DCM	–4.957	–2.436	2.521
$CHCl_3$	–4.840	–2.441	2.399
THF	–5.077	–2.434	2.643
Toluene	–4.957	–2.436	2.521

Table S39. Energy E (eV), wavelength λ (nm), and oscillator strength f of the lowest energy electronic transition (corresponding to the HOMO→LUMO monoelectronic excitation) calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] in the gas phase, DMSO, and DMF (SCRF IEF-PCM for complexes **1**–**6.**

	Gas			DMSO			DMF		
	E	λ	f	E	λ	f	E	λ	f
1	1.519	816	0.166	2.000	620	0.152	1.992	622	0.153
2	1.635	758	0.174	2.118	585	0.170	2.110	588	0.172
3	1.509	822	0.162	2.015	615	0.154	2.007	618	0.155
4	1.625	763	0.174	2.131	582	0.174	2.123	584	0.176
5	1.519	816	0.177	2.049	605	0.162	2.040	608	0.163
6	1.542	804	0.183	2.085	595	0.171	2.077	597	0.172

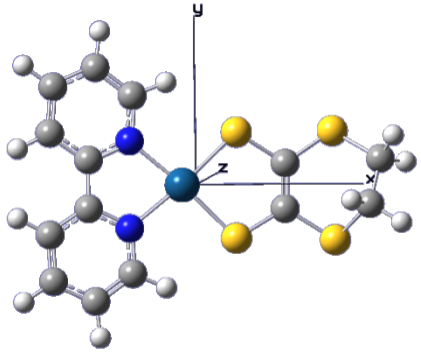
Table S40. Energy E (eV), wavelength λ (nm), and oscillator strength f of the lowest energy electronic transition (corresponding to the HOMO→LUMO monoelectronic excitation) calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] in different solvents (SCRF IEF-PCM) for complex **5**.

	E	λ	f
CH_3CN	2.044	607	0.157
DMSO	2.049	605	0.162
Acetone	2.045	615	0.160
DMF	2.040	608	0.163
DCM	1.932	642	0.169
$CHCl_3$	1.826	679	0.179
THF	1.907	650	0.170
Toluene	1.663	746	0.199

Table S41. Real (Re) and imaginary (Im) parts of second hyperpolarizability γ ($\times 10^{-31}$ esu) of complexes **1**–**6**, under 532 nm, 35 ps and 4 ns laser excitation.

	35 ps		4 ns	
	Reγ	Imγ	Reγ	Imγ
1	1.24±0.02	-	–(25.5±0.8)	–(12±0.6)
2	1.70±0.04	-	+(115±8)	–(148±28)
3	2.5±0.1	-	–(64±2)	-31±2
4	3.36±0.01	-	–(169±6)	-86±25
5	2.0±0.1	-	–(31.4±0.5)	–(16.3±2.0)
6	2.9±0.1	-	–(67±10)	–(38±2)

Table S42. Components of the dipole moment (Debye), linear polarizability (α), first hyperpolarizability (β), and second hyperpolarizability (γ) in a.u., and total values for α, β, and γ in a.u. and esu calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] for complex **1** in its input orientation (see below) in DMF (SCRF IEF-PCM).

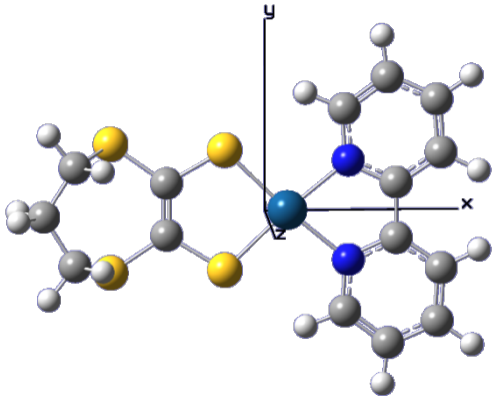


Dipole moment		Linear polarizability		First hyperpolarizabilty		Second hyperpolarizabilty	
μ_x	–15.136	α_{xx}	654.243	β_{xxx}	-2.757×10^4	γ_{xxxx}	8.129×10^6
μ_y	0.004	α_{yy}	479.634	β_{xxy}	2.008×10^2	γ_{yyyy}	3.482×10^5
μ_z	2.423	α_{zz}	190.459	β_{xyy}	-2.556×10^3	γ_{zzzz}	2.068×10^4
μ_{tot}	15.328	α_{tot}	441.445	β_{yyy}	7.046×10^1	γ_{xxyy}	6.095×10^5
		α (esu) × 10^{-24}	65.334	β_{xxz}	4.620×10^2	γ_{yyzz}	6.071×10^1
				β_{xyz}	–3.036	γ_{xxzz}	-2.085×10^4
				β_{yyz}	3.496×10^1	γ_{tot}	1.935×10^6
				β_{xzz}	-2.909×10^1	γ (esu) × 10^{-36}	974.6
				β_{yzz}	1.826×10^1		
				β_{zzz}	1.253×10^2		
				β_{tot}	3.017×10^4		
				β (esu) × 10^{-30}	260.7		

Table S43. Components of the dipole moment (Debye), linear polarizability (α), first hyperpolarizability (β), and second hyperpolarizability (γ) in a.u., and total values for α, β, and γ in a.u. and esu calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] for complex **1** in the dipole orientation in DMF (SCRF IEF-PCM).

Dipole moment		Linear polarizability		First hyperpolarizabilty		Second hyperpolarizabilty	
μ_x	0.000	α_{xx}	202.566	β_{xxx}	3.246×10^1	γ_{xxxx}	2.186×10^4
μ_y	0.000	α_{yy}	479.634	β_{xxy}	2.154×10^1	γ_{yyyy}	3.482×10^5
μ_z	15.328	α_{zz}	642.136	β_{xyy}	-3.695×10^2	γ_{zzzz}	7.802×10^6
μ_{tot}	15.328	α_{tot}	441.445	β_{yyy}	6.868×10^1	γ_{xxyy}	1.339×10^4
		α (esu) × 10^{-24}	65.334	β_{xxz}	5.857×10^2	γ_{yyzz}	5.968×10^5
				β_{xyz}	-2.425×10^1	γ_{xxzz}	1.420×10^5
				β_{yyz}	2.529×10^3	γ_{tot}	1.935×10^6
				β_{xzz}	-3.816×10^3	γ (esu) × 10^{-36}	974.7
				β_{yzz}	1.923×10^2		
				β_{zzz}	2.676×10^4		
				β_{tot}	3.017×10^4		
				β (esu) × 10^{-30}	260.7		

Table S44. Components of the dipole moment (Debye), linear polarizability (α), first hyperpolarizability (β), and second hyperpolarizability (γ) in a.u., and total values for α, β, and γ in a.u. and esu calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] for complex **2** in its input orientation (see below) in DMF (SCRF IEF-PCM).

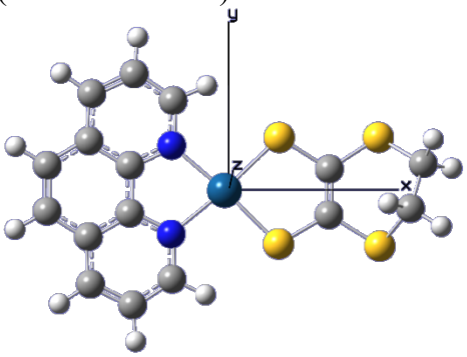


Dipole moment		Linear polarizability		First hyperpolarizabilty		Second hyperpolarizabilty	
μ_x	15.104	α_{xx}	673.149	β_{xxx}	2.410×10^{4}	γ_{xxxx}	6.285×10^{6}
μ_y	0.001	α_{yy}	493.141	β_{xxy}	3.929×10^{-1}	γ_{yyyy}	3.483×10^{5}
μ_z	4.060	α_{zz}	214.243	β_{xyy}	2.240×10^{3}	γ_{zzzz}	2.398×10^{4}
μ_{tot}	15.640	α_{tot}	460.178	β_{yyy}	1.628×10^{-1}	γ_{xxyy}	5.858×10^{5}
		α (esu) $\times 10^{-24}$	68.106	β_{xxz}	1.307×10^{3}	γ_{yyzz}	9.104×10^{2}
				β_{xyz}	1.324×10^{-1}	γ_{xxzz}	-4.571×10^{3}
				β_{yyz}	1.476×10^{2}	γ_{tot}	1.564×10^{6}
				β_{xzz}	2.781×10^{1}	γ (esu) $\times 10^{-36}$	787.9
				β_{yzz}	4.081×10^{-2}		
				β_{zzz}	1.738×10^{2}		
				β_{tot}	2.641×10^{4}		
				β (esu) $\times 10^{-30}$	228.2		

Table S45. Components of the dipole moment (Debye), linear polarizability (α), first hyperpolarizability (β), and second hyperpolarizability (γ) in a.u., and total values for α, β, and γ in a.u. and esu calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] for complex **2** in the dipole orientation in DMF (SCRF IEF-PCM).

Dipole moment		Linear polarizability		First hyperpolarizabilty		Second hyperpolarizabilty	
μ_x	0.000	α_{xx}	243.749	β_{xxx}	3.004×10^{1}	γ_{xxxx}	3.987×10^{4}
μ_y	0.000	α_{yy}	493.141	β_{xxy}	-1.375×10^{-1}	γ_{yyyy}	3.483×10^{5}
μ_z	15.640	α_{zz}	643.643	β_{xyy}	4.389×10^{2}	γ_{zzzz}	5.716×10^{6}
μ_{tot}	15.640	α_{tot}	460.178	β_{yyy}	-2.910×10^{-1}	γ_{xxyy}	2.945×10^{4}
		α (esu) $\times 10^{-24}$	68.106	β_{xxz}	1.022×10^{3}	γ_{yyzz}	5.576×10^{5}
				β_{xyz}	-4.536×10^{-1}	γ_{xxzz}	2.719×10^{5}
				β_{yyz}	2.202×10^{3}	γ_{tot}	1.565×10^{6}
				β_{xzz}	4.802×10^{3}	γ (esu) $\times 10^{-36}$	788.0
				β_{yzz}	-7.466×10^{-1}		
				β_{zzz}	2.266×10^{4}		
				β_{tot}	2.641×10^{4}		
				β (esu) $\times 10^{-30}$	228.2		

Table S46. Components of the dipole moment (Debye), linear polarizability (α), first hyperpolarizability (β), and second hyperpolarizability (γ) in a.u., and total values for α, β, and γ in a.u. and esu calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] for complex **3** in its input orientation (see below) in DMF (SCRF IEF-PCM).

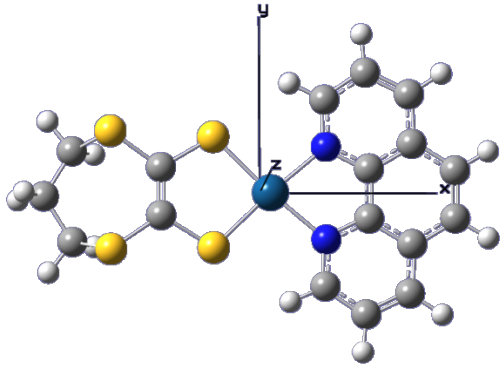


Dipole moment		Linear polarizability		First hyperpolarizabilty		Second hyperpolarizabilty	
μ_x	–15.660	α_{xx}	710.527	β_{xxx}	-2.852×10^4	γ_{xxxx}	8.773×10^6
μ_y	0.010	α_{yy}	535.266	β_{xxy}	2.526×10^2	γ_{yyyy}	2.687×10^5
μ_z	2.404	α_{zz}	197.330	β_{xyy}	-3.443×10^3	γ_{zzzz}	2.068×10^4
μ_{tot}	15.844	α_{tot}	481.041	β_{yyy}	7.654×10^1	γ_{xxyy}	9.330×10^5
		α (esu) × 10^{-24}	71.194	β_{xxz}	3.913×10^2	γ_{yyzz}	-1.945×10^3
				β_{xyz}	-2.138×10^1	γ_{xxzz}	-2.263×10^4
				β_{yyz}	3.085×10^1	γ_{tot}	2.176×10^6
				β_{xzz}	-1.814×10^1	γ (esu) × 10^{-36}	1096
				β_{yzz}	2.011×10^1		
				β_{zzz}	1.257×10^2		
				β_{tot}	3.199×10^4		
				β (esu) × 10^{-30}	276.4		

Table S47. Components of the dipole moment (Debye), linear polarizability (α), first hyperpolarizability (β), and second hyperpolarizability (γ) in a.u., and total values for α, β, and γ in a.u. and esu calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] for complex **3** in the dipole orientation in DMF (SCRF IEF-PCM).

Dipole moment		Linear polarizability		First hyperpolarizabilty		Second hyperpolarizabilty	
μ_x	0.000	α_{xx}	209.877	β_{xxx}	4.044×10^1	γ_{xxxx}	2.176×10^4
μ_y	0.000	α_{yy}	535.265	β_{xxy}	1.814×10^1	γ_{yyyy}	2.686×10^5
μ_z	15.844	α_{zz}	697.981	β_{xyy}	-4.920×10^2	γ_{zzzz}	8.436×10^6
μ_{tot}	15.844	α_{tot}	481.041	β_{yyy}	7.091×10^1	γ_{xxyy}	1.707×10^4
		α (esu) × 10^{-24}	71.194	β_{xxz}	5.698×10^2	γ_{yyzz}	9.154×10^5
				β_{xyz}	-1.083×10^1	γ_{xxzz}	1.455×10^5
				β_{yyz}	3.408×10^3	γ_{tot}	2.176×10^6
				β_{xzz}	-3.860×10^3	γ (esu) × 10^{-36}	1096
				β_{yzz}	2.426×10^2		
				β_{zzz}	2.772×10^4		
				β_{tot}	3.199×10^4		
				β (esu) × 10^{-30}	276.4		

Table S48. Components of the dipole moment (Debye), linear polarizability (α), first hyperpolarizability (β), and second hyperpolarizability (γ) in a.u., and total values for α, β, and γ in a.u. and esu calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] for complex **4** in its input orientation (see below) in DMF (SCRF IEF-PCM).

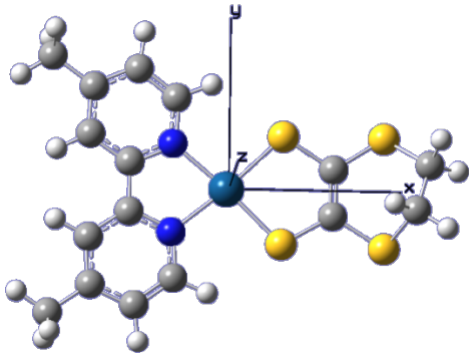


Dipole moment		Linear polarizability		First hyperpolarizabilty		Second hyperpolarizabilty	
μ_x	15.603	α_{xx}	730.684	β_{xxx}	2.526×10^{4}	γ_{xxxx}	6.949×10^{6}
μ_y	0.000	α_{yy}	548.965	β_{xxy}	-2.712×10^{-1}	γ_{yyyy}	2.657×10^{5}
μ_z	–3.900	α_{zz}	220.782	β_{xyy}	3.087×10^{3}	γ_{zzzz}	2.417×10^{4}
μ_{tot}	16.083	α_{tot}	500.144	β_{yyy}	-3.322×10^{-2}	γ_{xxyy}	8.807×10^{5}
		α (esu) × 10^{-24}	74.021	β_{xxz}	-1.139×10^{3}	γ_{yyzz}	-1.098×10^{3}
				β_{xyz}	1.425×10^{-1}	γ_{xxzz}	-9.125×10^{3}
				β_{yyz}	-1.556×10^{2}	γ_{tot}	1.796×10^{6}
				β_{xzz}	2.106	γ (esu) × 10^{-36}	904.6
				β_{yzz}	-2.841×10^{-2}		
				β_{zzz}	-1.808×10^{2}		
				β_{tot}	2.838×10^{4}		
				β (esu) × 10^{-30}	245.3		

Table S49. Components of the dipole moment (Debye), linear polarizability (α), first hyperpolarizability (β), and second hyperpolarizability (γ) in a.u., and total values for α, β, and γ in a.u. and esu calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] for complex **4** in the dipole orientation in DMF (SCRF IEF-PCM).

Dipole moment		Linear polarizability		First hyperpolarizabilty		Second hyperpolarizabilty	
μ_x	0.000	α_{xx}	250.174	β_{xxx}	1.562	γ_{xxxx}	3.821×10^{4}
μ_y	0.000	α_{yy}	548.965	β_{xxy}	-7.049×10^{-2}	γ_{yyyy}	2.657×10^{5}
μ_z	16.083	α_{zz}	701.293	β_{xyy}	5.977×10^{2}	γ_{zzzz}	6.368×10^{6}
μ_{tot}	16.083	α_{tot}	500.144	β_{yyy}	-1.526×10^{-1}	γ_{xxyy}	3.745×10^{4}
		α (esu) × 10^{-24}	74.021	β_{xxz}	9.801×10^{2}	γ_{yyzz}	8.432×10^{5}
				β_{xyz}	-2.097×10^{-1}	γ_{xxzz}	2.747×10^{5}
				β_{yyz}	3.033×10^{3}	γ_{tot}	1.796×10^{6}
				β_{xzz}	4.843×10^{3}	γ (esu) × 10^{-36}	904.8
				β_{yzz}	-1.387×10^{-2}		
				β_{zzz}	2.384×10^{4}		
				β_{tot}	2.838×10^{4}		
				β (esu) × 10^{-30}	245.3		

Table S50. Components of the dipole moment (Debye), linear polarizability (α), first hyperpolarizability (β), and second hyperpolarizability (γ) in a.u., and total values for α, β, and γ in a.u. and esu calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] for complex **5** in its input orientation (see below) in DMF (SCRF IEF-PCM).

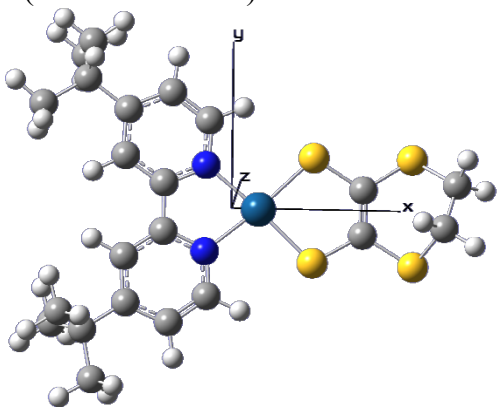


Dipole moment		Linear polarizability		First hyperpolarizabilty		Second hyperpolarizabilty	
μ_x	–16.916	α_{xx}	699.526	β_{xxx}	-2.682×10^4	γ_{xxxx}	8.282×10^6
μ_y	–0.008	α_{yy}	521.013	β_{xxy}	1.735×10^2	γ_{yyyy}	4.116×10^5
μ_z	2.420	α_{zz}	215.618	β_{xyy}	-2.381×10^3	γ_{zzzz}	2.186×10^4
μ_{tot}	17.089	α_{tot}	478.719	β_{yyy}	5.828×10^1	γ_{xxyy}	6.844×10^5
		α (esu) × 10^{-24}	70.850	β_{xxz}	3.670×10^2	γ_{yyzz}	3.178×10^3
				β_{xyz}	-1.478×10^1	γ_{xxzz}	-1.785×10^4
				β_{yyz}	2.310×10^1	γ_{tot}	2.011×10^6
				β_{xzz}	-7.175×10^1	γ (esu) × 10^{-36}	1013
				β_{yzz}	1.877×10^1		
				β_{zzz}	1.293×10^2		
				β_{tot}	2.928×10^4		
				β (esu) × 10^{-30}	253.0		

Table S51. Components of the dipole moment (Debye), linear polarizability (α), first hyperpolarizability (β), and second hyperpolarizability (γ) in a.u., and total values for α, β, and γ in a.u. and esu calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] for complex **5** in the dipole orientation in DMF (SCRF IEF-PCM).

Dipole moment		Linear polarizability		First hyperpolarizabilty		Second hyperpolarizabilty	
μ_x	0.000	α_{xx}	226.145	β_{xxx}	4.114×10^1	γ_{xxxx}	2.286×10^4
μ_y	0.000	α_{yy}	521.015	β_{xxy}	1.825×10^1	γ_{yyyy}	4.116×10^5
μ_z	17.089	α_{zz}	688.997	β_{xyy}	-3.144×10^2	γ_{zzzz}	8.006×10^6
μ_{tot}	17.089	α_{tot}	478.719	β_{yyy}	6.130×10^1	γ_{xxyy}	1.532×10^4
		α (esu) × 10^{-24}	70.850	β_{xxz}	5.165×10^2	γ_{yyzz}	6.731×10^5
				β_{xyz}	–9.749	γ_{xxzz}	1.191×10^5
				β_{yyz}	2.360×10^3	γ_{tot}	2.011×10^6
				β_{xzz}	-3.359×10^3	γ (esu) × 10^{-36}	1013
				β_{yzz}	1.835×10^2		
				β_{zzz}	2.618×10^4		
				β_{tot}	2.928×10^4		
				β (esu) × 10^{-30}	253.0		

Table S52. Components of the dipole moment (Debye), linear polarizability (α), first hyperpolarizability (β), and second hyperpolarizability (γ) in a.u., and total values for α, β, and γ in a.u. and esu calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] for complex **6** in its input orientation (see below) in DMF (SCRF IEF-PCM).

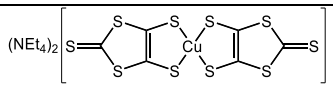
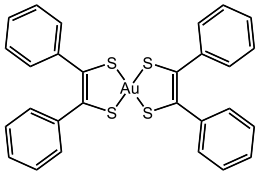
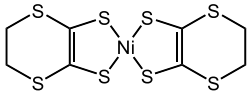
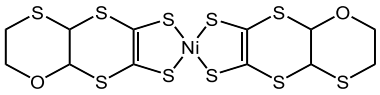
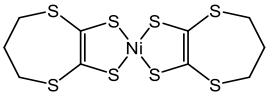
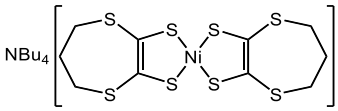
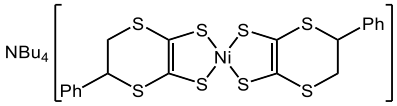
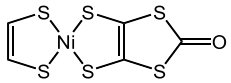
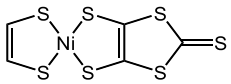
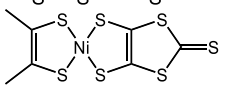
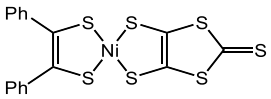
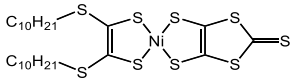
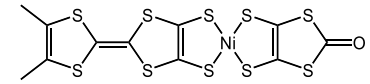
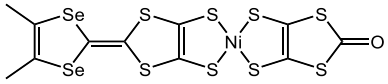
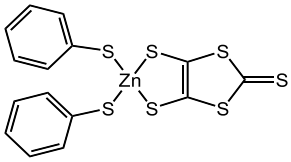
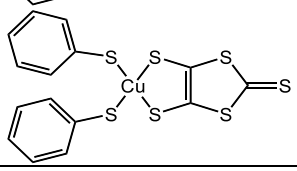


Dipole moment		Linear polarizability		First hyperpolarizabilty		Second hyperpolarizabilty	
μ_x	–17.554	α_{xx}	800.015	β_{xxx}	-2.654×10^4	γ_{xxxx}	8.262×10^6
μ_y	–0.036	α_{yy}	612.318	β_{xxy}	3.664×10^2	γ_{yyyy}	4.586×10^5
μ_z	2.359	α_{zz}	306.518	β_{xyy}	-2.538×10^3	γ_{zzzz}	4.100×10^4
μ_{tot}	17.711	α_{tot}	572.950	β_{yyy}	9.690×10^1	γ_{xxyy}	7.417×10^5
		α (esu) × 10^{-24}	84.797	β_{xxz}	2.577×10^2	γ_{yyzz}	1.055×10^4
				β_{xyz}	-3.275×10^1	γ_{xxzz}	-3.845×10^3
				β_{yyz}	1.696×10^1	γ_{tot}	2.052×10^6
				β_{xzz}	-5.817×10^1	γ (esu) × 10^{-36}	1033
				β_{yzz}	-1.185×10^2		
				β_{zzz}	1.221×10^2		
				β_{tot}	2.914×10^4		
				β (esu) × 10^{-30}	251.8		

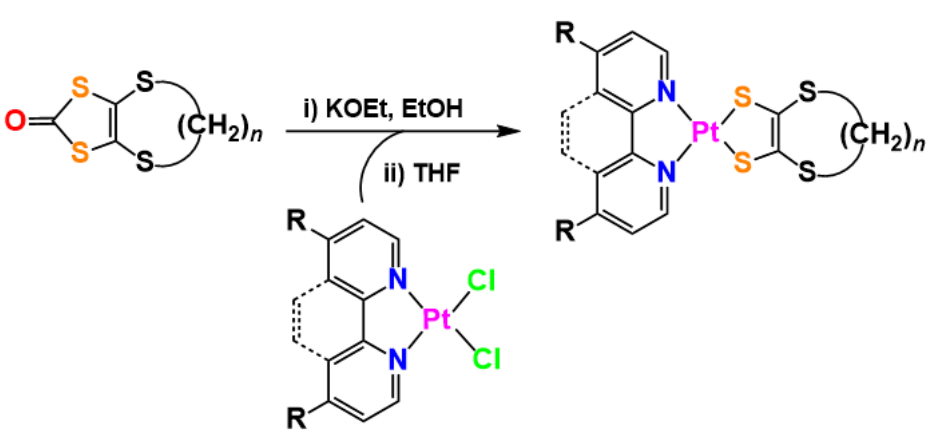
Table S53. Components of the dipole moment (Debye), linear polarizability (α), first hyperpolarizability (β), and second hyperpolarizability (γ) in a.u., and total values for α, β, and γ in a.u. and esu calculated at the DFT level [PBE0//cc-pVDZ/LANL08(f)] for complex **6** in the dipole orientation in DMF (SCRF IEF-PCM).

Dipole moment		Linear polarizability		First hyperpolarizabilty		Second hyperpolarizabilty	
μ_x	0.000	α_{xx}	316.627	β_{xxx}	4.750×10^1	γ_{xxxx}	4.254×10^4
μ_y	0.000	α_{yy}	612.332	β_{xxy}	-1.164×10^2	γ_{yyyy}	4.587×10^5
μ_z	17.712	α_{zz}	789.892	β_{xyy}	-3.221×10^2	γ_{zzzz}	8.004×10^6
μ_{tot}	17.712	α_{tot}	572.950	β_{yyy}	1.106×10^2	γ_{xxyy}	2.279×10^4
		α (esu) × 10^{-24}	84.797	β_{xxz}	4.709×10^2	γ_{yyzz}	7.305×10^5
				β_{xyz}	-4.201×10^1	γ_{xxzz}	1.240×10^5
				β_{yyz}	2.519×10^3	γ_{tot}	2.052×10^6
				β_{xzz}	-3.214×10^3	γ (esu) × 10^{-36}	1034
				β_{yzz}	4.034×10^2		
				β_{zzz}	2.594×10^4		
				β_{tot}	2.914×10^4		
				β (esu) × 10^{-30}	251.8		

Table S54. Second hyperpolarizabilities of 1,2-dithiolene complexes obtained at 532 nm excitation wavelength under picosecond or nanosecond laser pulses by using the Z-scan or degenerate four-wave mixing (DFWM) techniques.

Complex	Experimental technique	Laser pulses	Solvent	γ ($\times 10^{-29}$ esu)	Ref.
	Z-scan	28 ps	Acetone	0.0517	1
	Z-scan	4 ns	CS_2	0.55	2
	Z-scan	8 ns	CS_2	3.7	3
	Z-scan	40 ps	DMF	0.014	4
	Z-scan	8 ns	CS_2	6.3	3
	Z-scan	40 ps	CS_2	0.045	4
	Z-scan	8 ns	CS_2	1.4	3
	Z-scan	40 ps	DMF	0.0024	4
	Z-scan	200 ps	–	0.71	5
	Z-scan	200 ps	–	0.81	5
	Z-scan	8 ns	CS_2	3.5	6
	Z-scan	8 ns	CS_2	3.8	6
	Z-scan	8 ns	CS_2	3.6	6
	Z-scan	8 ns	CS_2	2.2	6
	Z-scan	8 ns	CS_2	2.6	6
	Z-scan	8 ns	CS_2	2.3	7
	Z-scan	8 ns	CS_2	3.7	7
	DFWM	15 ps	Acetone	0.263	8
	DFWM	15 ps	Acetone	0.280	8

2. Schemes and Figures



	N^N	R	*n*
1	bipy	H	2
2	phen	H	3
3	bipy	H	2
4	phen	H	3
5	bipy	Me	2
6	bipy	^{t}Bu	2

Scheme S1. Synthetic route for the preparation of compounds **1**–**6**.

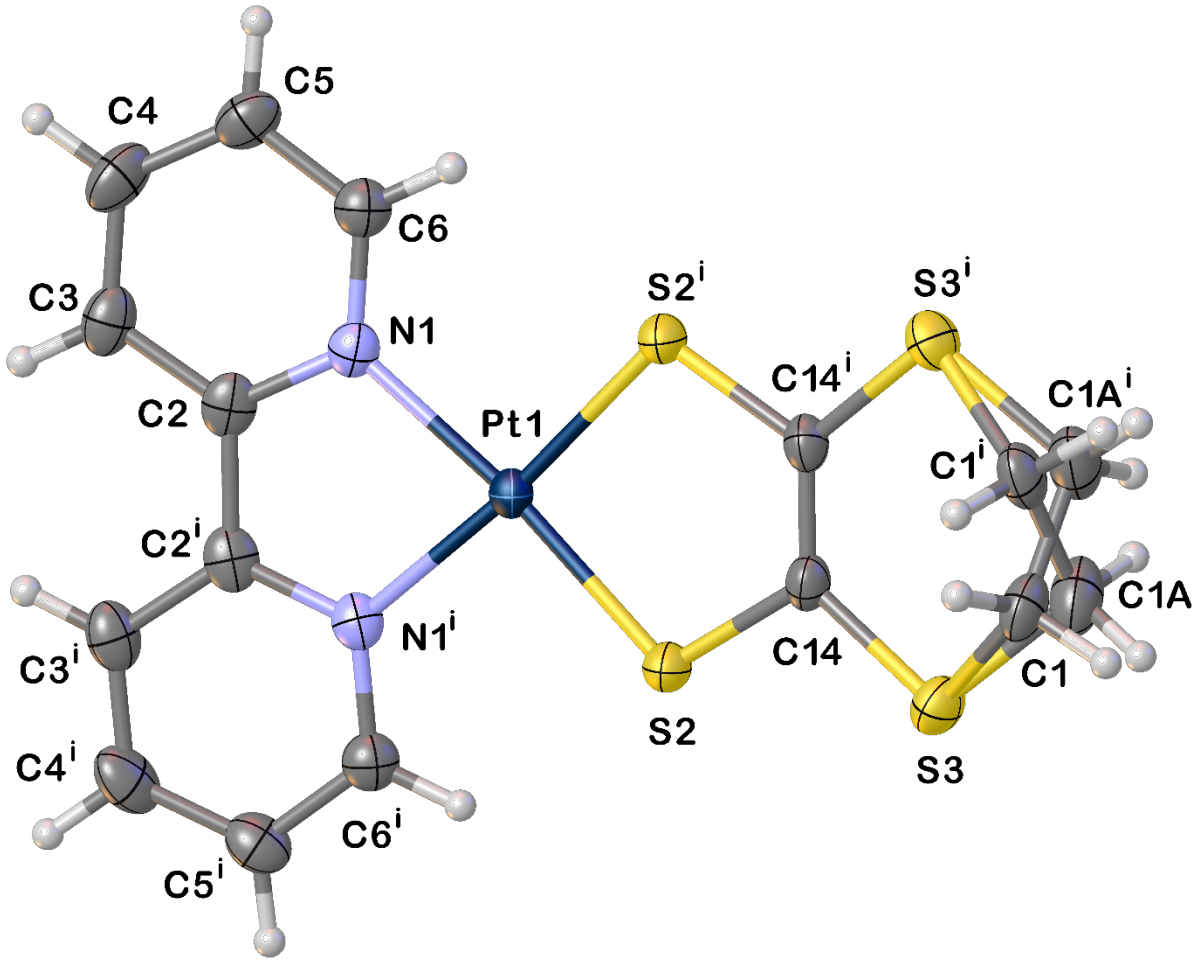


Figure S1. Drawing and atom labeling scheme for complex **1**, showing the disorder on the terminal carbons of the $dddt^{2-}$ 1,2-dithiolene ligand modelled over two positions. ^{i} : +x, 3/2−y, +z.

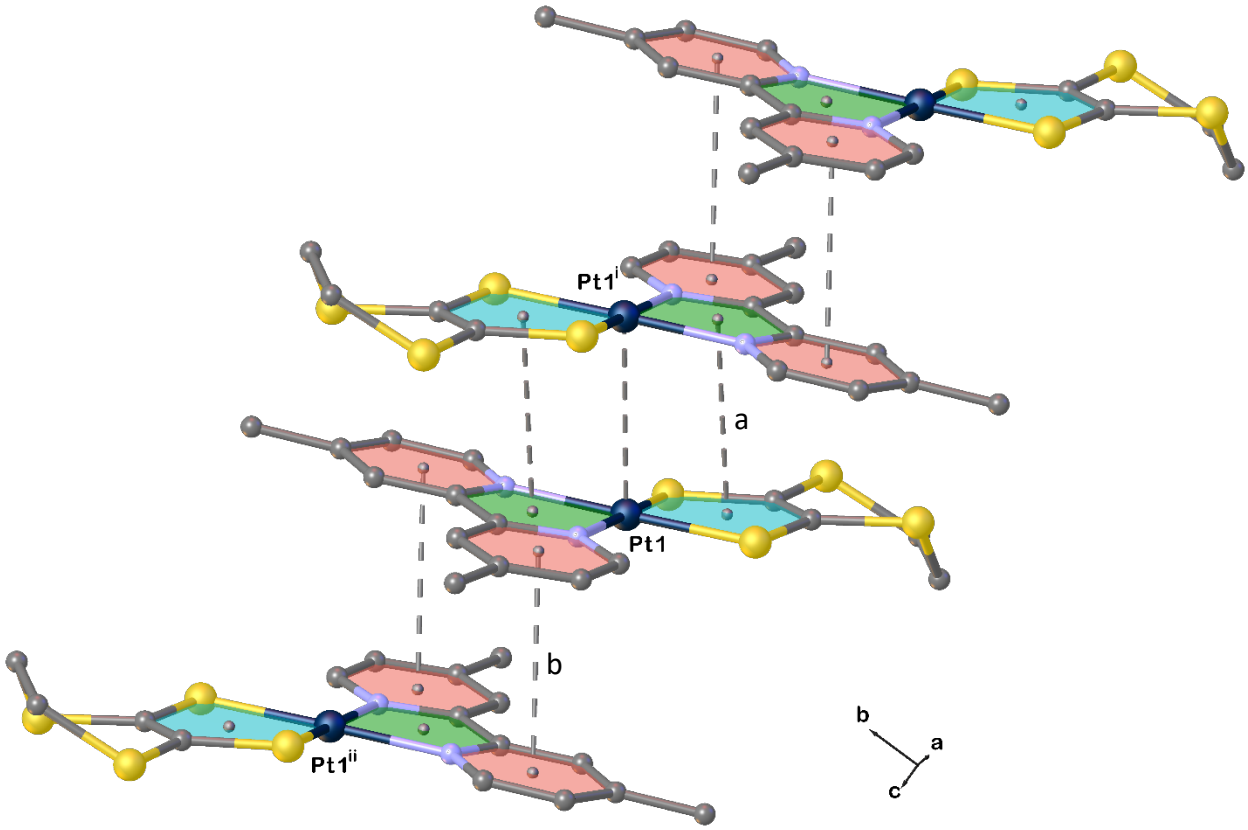


Figure S2. Perspective drawing of the interacting symmetry-related molecular units in the crystal structure of complex **5**. Intercentroid distance (a) 3.74; (b) 3.64 Å; Pt···Pt^{i} distance 3.77 Å. Hydrogen atoms have been omitted for clarity. Symmetry operations: ^{i} = 1–x, 1–y, 1–z; ^{ii} = x, y, −1+z.

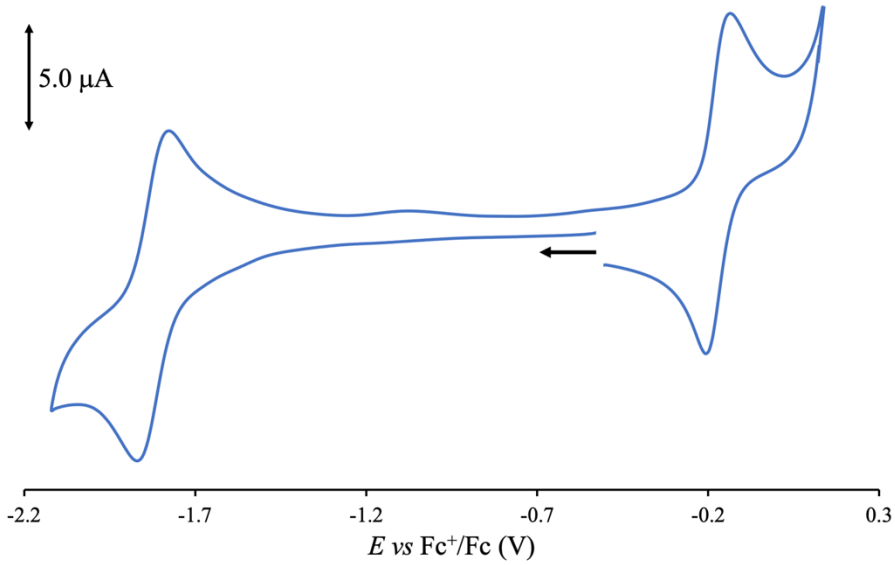


Figure S3. Cyclic voltammogram recorded for an anhydrous DMSO solution of complex **5** (298 K; scan rate 100 mV s^{-1}; 0.1 M $TBAPF_6$).

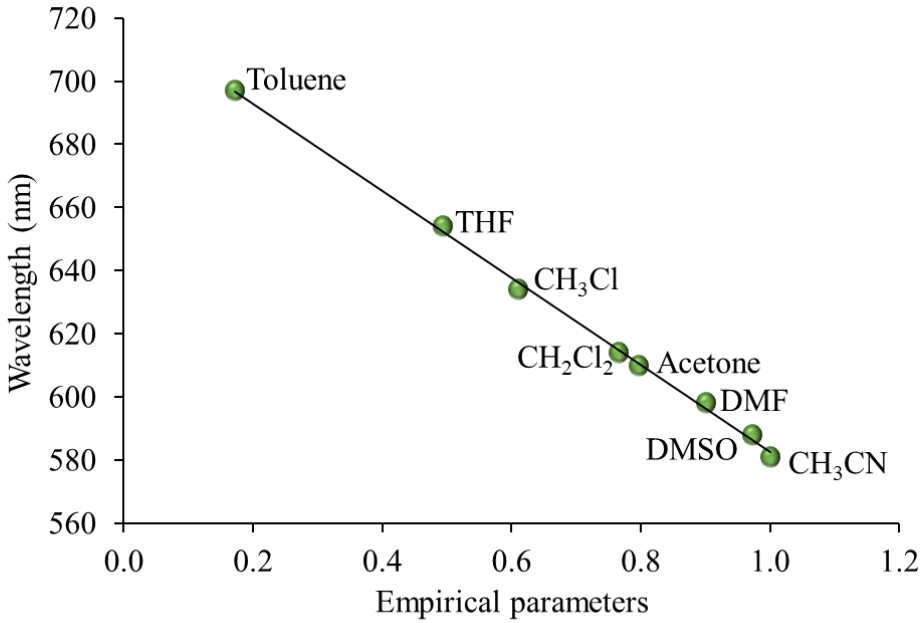


Figure S4. Correlation between Eisenberg empirical parameters[9] and experimentally measured λ_{max} visible absorption maxima recorded for complex **3** in eight solvents ($R^2 = 0.998$).

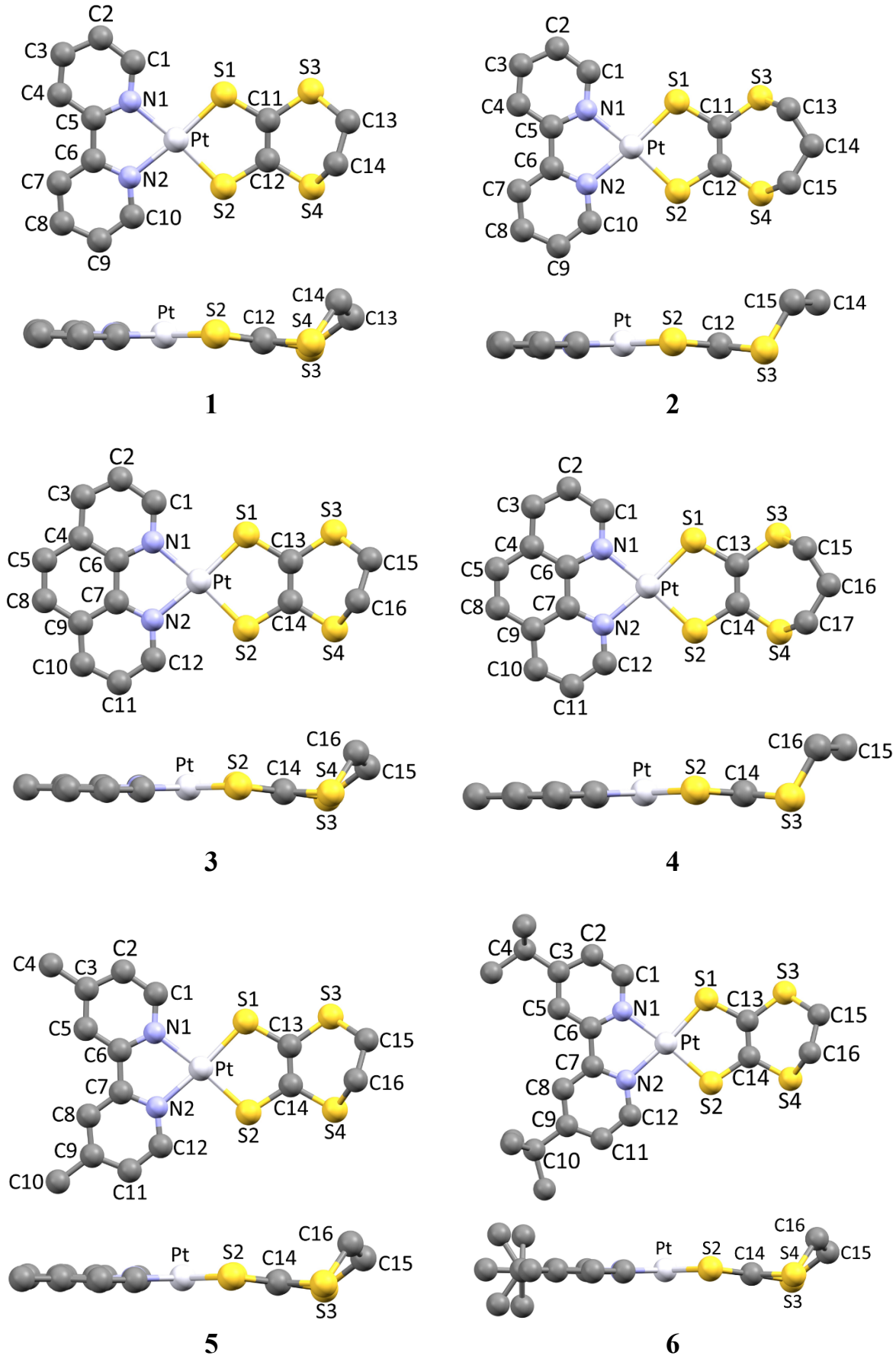


Figure S5. Different perspectives of the geometries optimised for complexes **1**–**6** at the DFT level [PBE0//cc-pVDZ/LANL08(f)] in the gas phase. Hydrogen atoms were omitted for clarity.

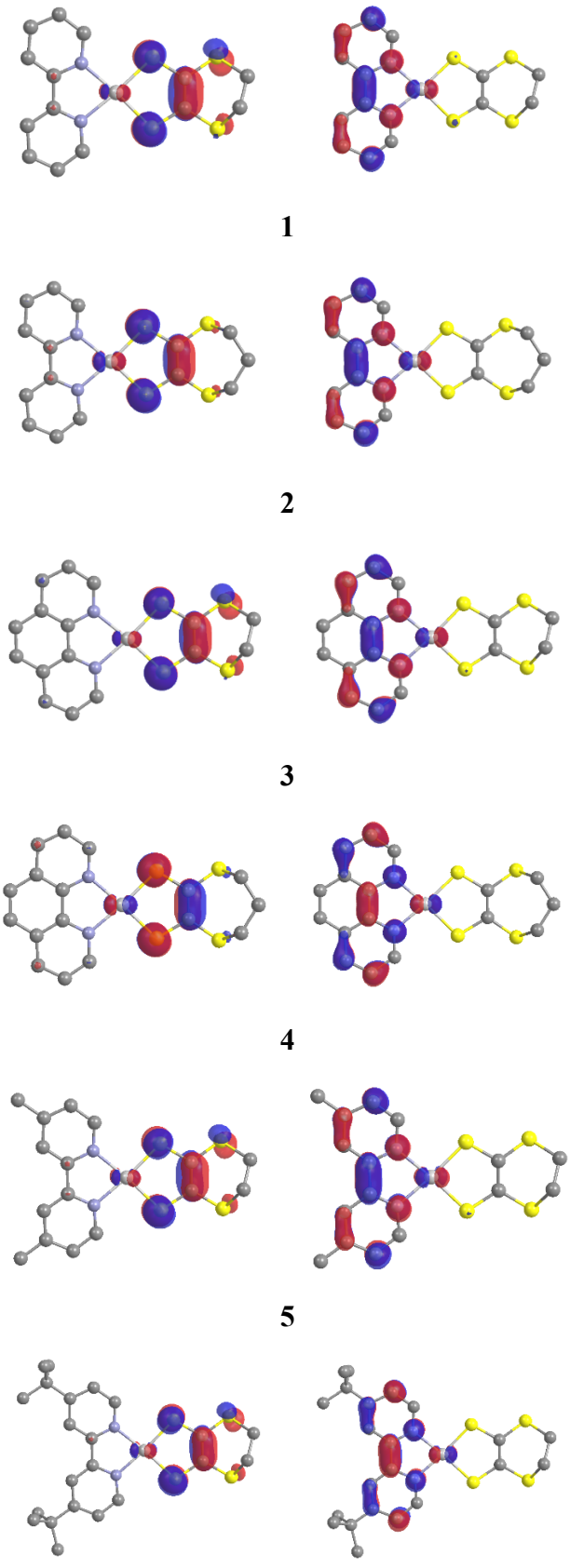


Figure S6. KS-HOMO (left) and KS-LUMO (right) calculated for complexes **1–6** at the DFT level [PBE0//cc-pVDZ/LANL08(f)] in the gas phase. Hydrogen atoms were omitted for clarity. Isovalue 0.05 |e|.

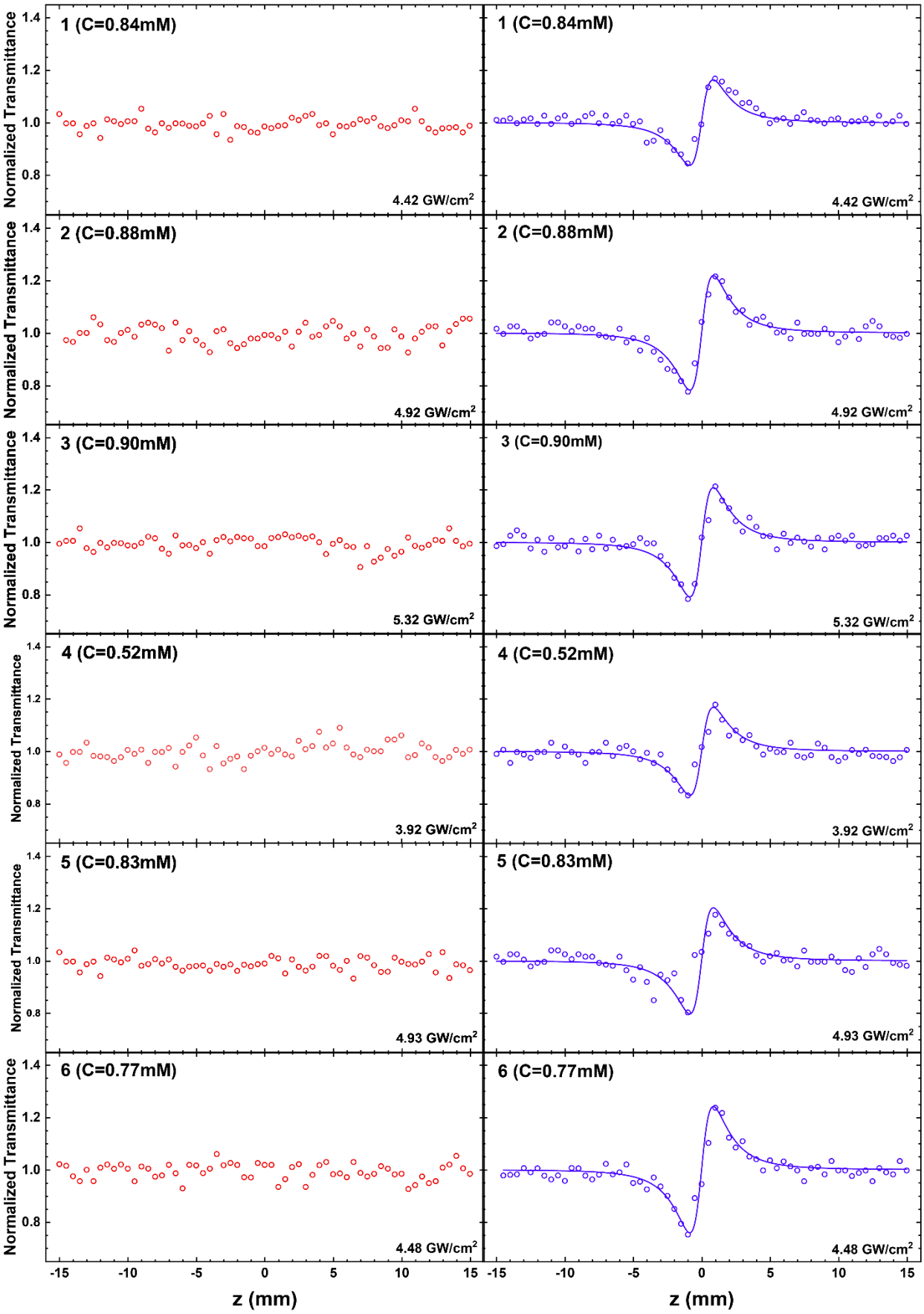


Figure S7. "Open-aperture" (left) and "divided" (right) Z-scans of complexes **1**–**6** obtained from the Z-scan measurements under 35 ps, 532 nm laser excitation.

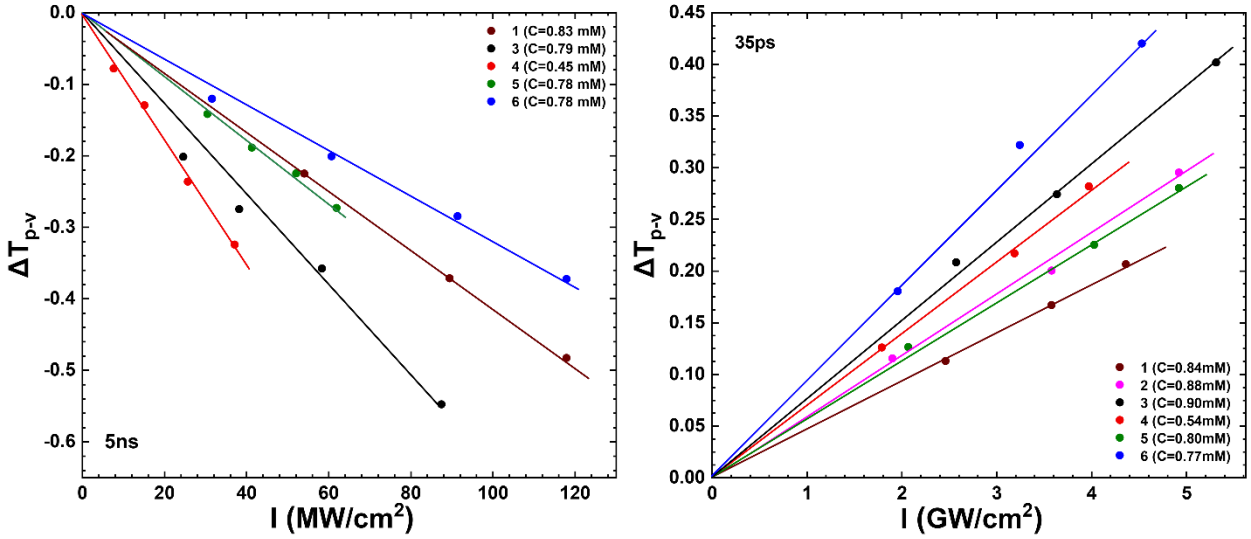


Figure S8. Variation of the ΔT_{p-v} parameter with the incident laser intensity under 4 ns (left) and 35 ps (right), 532 nm laser excitation conditions.

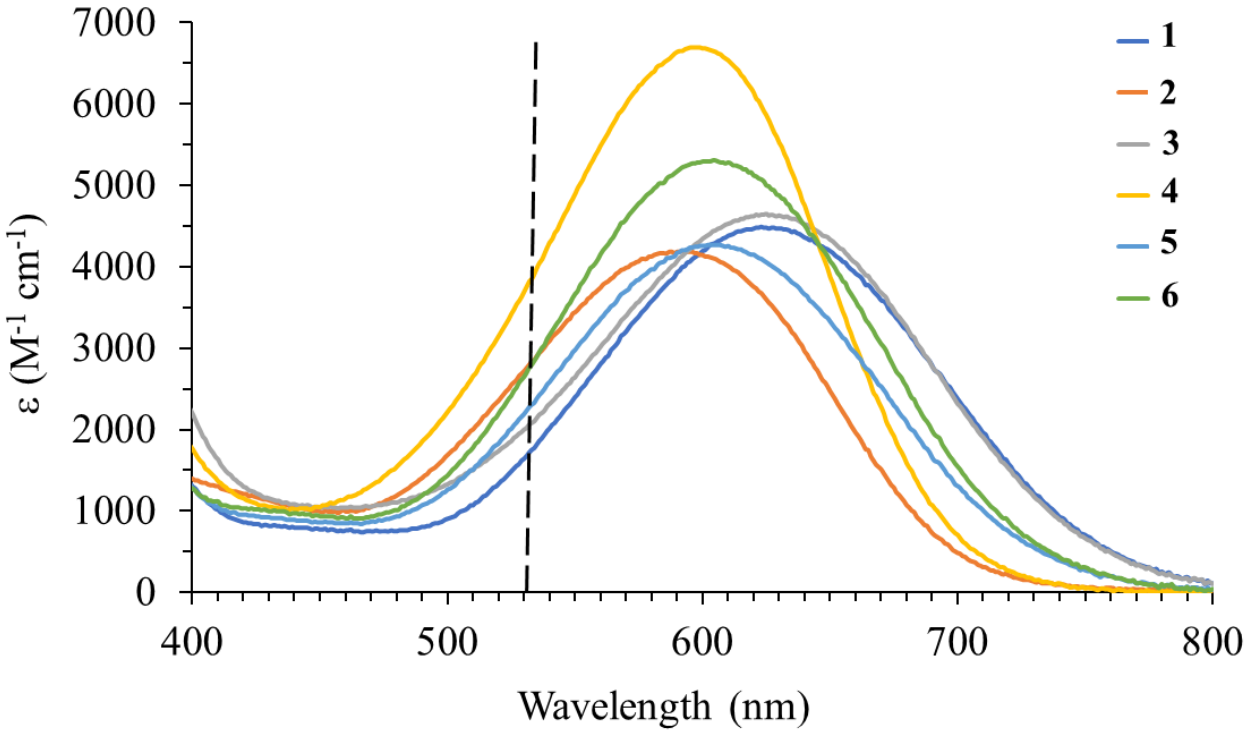


Figure S9. Absorption spectra in the visible region (400–800 nm) recorded for complexes **1**–**6** in DMF; the dotted line at λ = 532 nm indicates the laser excitation wavelength; molar extinction coefficients at 532 nm ε_{532} = 1700 (complex **1**), 2800 (**2**), 2100 (**3**), 3800 (**4**), 2300 (**5**), and 2700 (**6**) $M^{-1}\cdot cm^{-1}$.

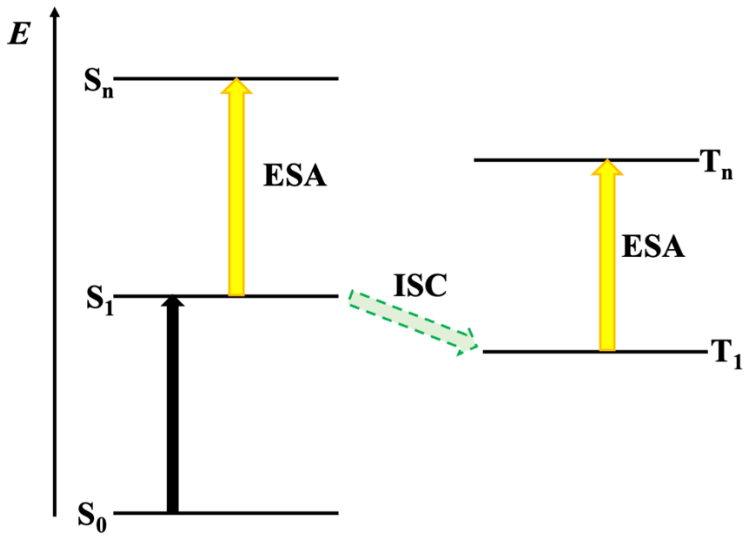


Figure S10. Schematic representation of the five-level model[10] for the interpretation of NLO absorption: the initial linear absorption promotes the system from the ground state S_0 to the first singlet excited state S_1. An intersystem crossing (ISC) to the triplet state T_1 can occur. Nonlinear absorption is observed when further excitations $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$ take place (excited state absorption, ESA).

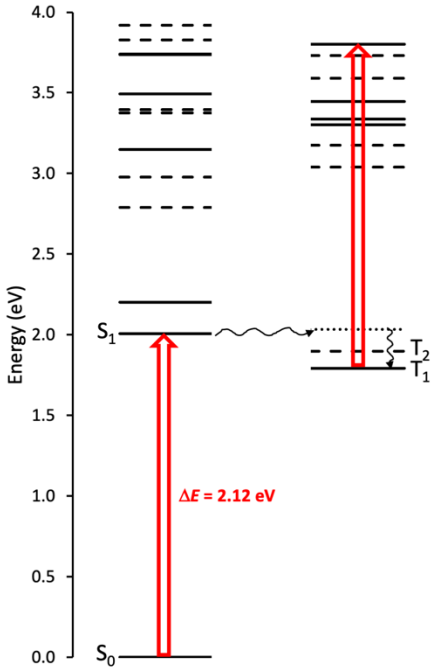


Figure S11. Jablonski diagram (0.0–4.0 eV) calculated for complex **4** at TD-DFT level [PBE0//cc-pVDZ/LANL08(f)] in DMF (SCRF IEF-PCM). Excited states calculated for the $S_0 \rightarrow S_n$ and $T_1 \rightarrow T_n$ transitions with oscillator strength values $f < 0.05$ are represented as dashed lines. Red arrows represent energy gaps corresponding to the $S_0 \rightarrow S_1$ transition; wavy arrows correspond to the internal conversion of S_1, ISC between S_1 and the triplet state optimised at the same geometry (dotted line), and the internal conversion leading from the former to T_1.

3. References

1 X. Q. Wang, Q. Ren, F. J. Zhang, W. F. Guo, X. B. Sun, J. Sun, H. L. Yang, G. H. Zhang, X. Q. Hou and D. Xu, *Mater. Res. Bull.*, 2008, **43**, 2342–2353.

2 G. Chatzikyriakos, I. Papagiannouli, S. Couris, G. C. Anyfantis and G. C. Papavassiliou, *Chem. Phys. Lett.*, 2011, **513**, 229–235.

3 P. Aloukos, G. Chatzikyriakos, I. Papagiannouli, N. Liaros and S. Couris, *Chem. Phys. Lett.*, 2010, **495**, 245–250.

4 G. Soras, N. Psaroudakis, G. A. Mousdis, M. J. Manos, A. J. Tasiopoulos, P. Aloukos, S. Couris, P. Labéguerie, J. Lipinski, A. Avramopoulos and M. G. Papadopoulos, *Chem. Phys.*, 2010, **372**, 33–45.

5 J.-L. Zuo, T.-M. Yao, F. You, X.-Z. You, H.-K. Funb and B.-C. Yipb, *J. Mater. Chem.*, 1996, **6**, 1633–1637.

6 P. Aloukos, S. Couris, J. B. Koutselas, G. C. Anyfantis and G. C. Papavassiliou, *Chem. Phys. Lett.*, 2006, **428**, 109–113.

7 G. C. Anyfantis, G. C. Papavassiliou, P. Aloukos, S. Couris, Y. F. Weng, H. Yoshino and K. Murata, *Zeitschrift für Naturforsch. B*, 2007, **62**, 200–204.

8 J. Dai, G. Q. Bian, X. Wang, Q. F. Xu, M. Y. Zhou, M. Munakata, M. Maekawa, M. H. Tong, Z. R. Sun and H. P. Zeng, *J. Am. Chem. Soc.*, 2000, **122**, 11007–11008.

9 S. D. Cummings and R. Eisenberg, *J. Am. Chem. Soc.*, 1996, **118**, 1949–1960.

10 B. J. Thompson, *Handbook of nonlinear optics*, Marcel Dekker, Inc., New York, 1996.