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Peripheral functionalisation of a stable phthalocyanine J-type dimer to control the aggregation behaviour and NLO properties: UV–Vis, fluorescence, DFT, TDHF and thermal study

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1. MALDI–TOF/TOF mass spectra

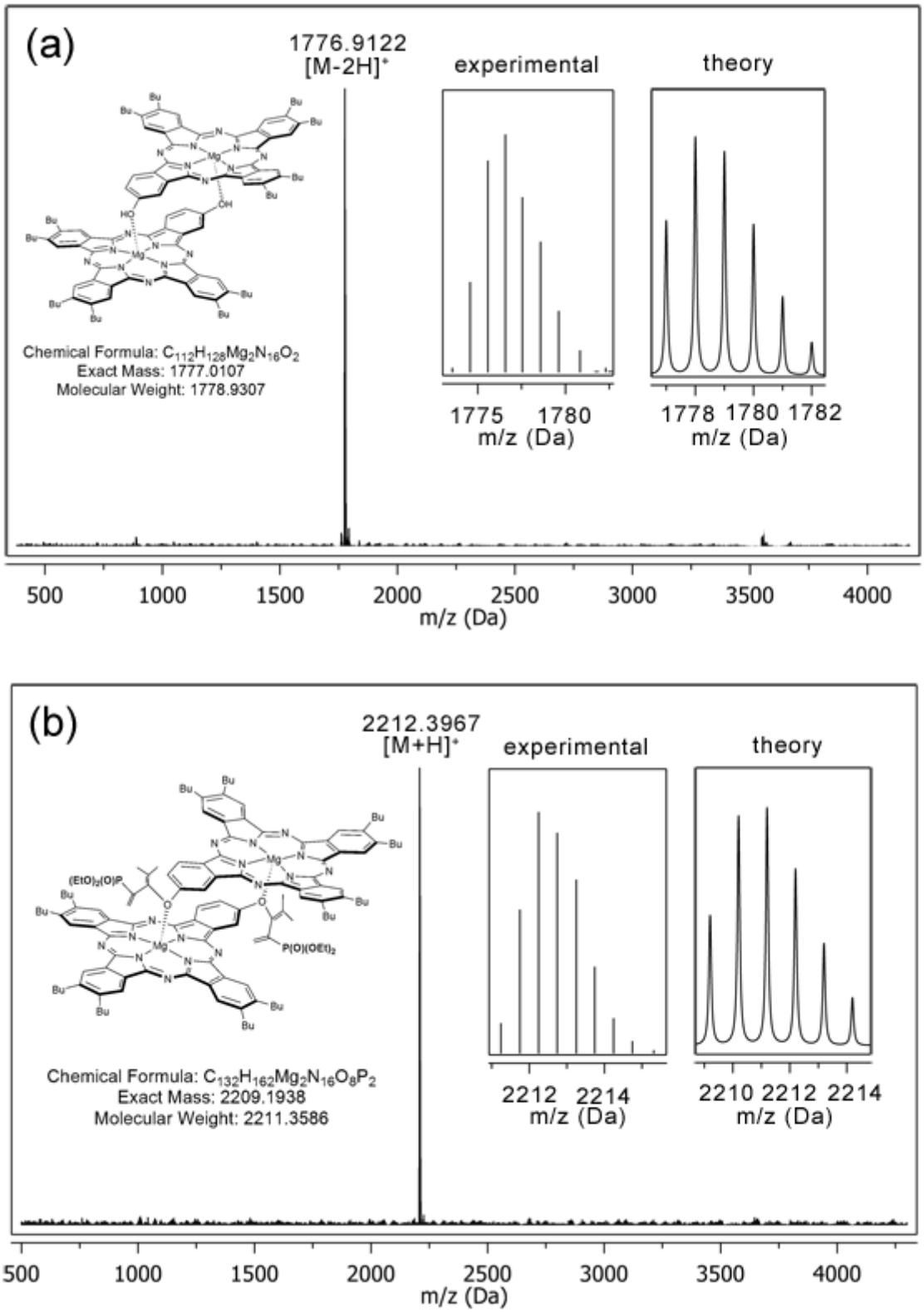

Fig. S1. MALDI–TOF/TOF mass spectra of **2** (a, no matrix) and **4** (b, matrix – DHB).

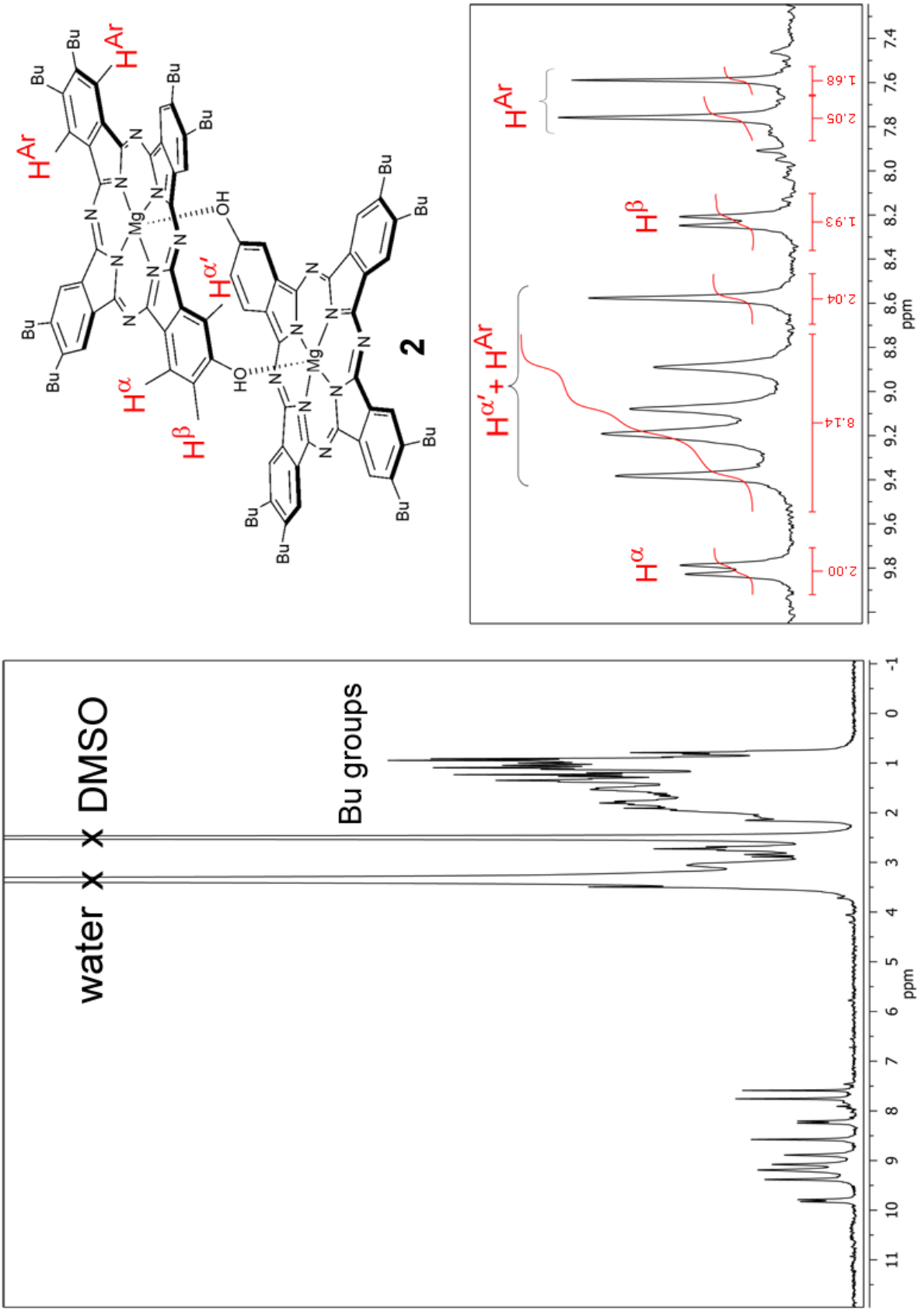

Fig S2. ^{1}H NMR spectrum (DMSO-d_6) of **2**.

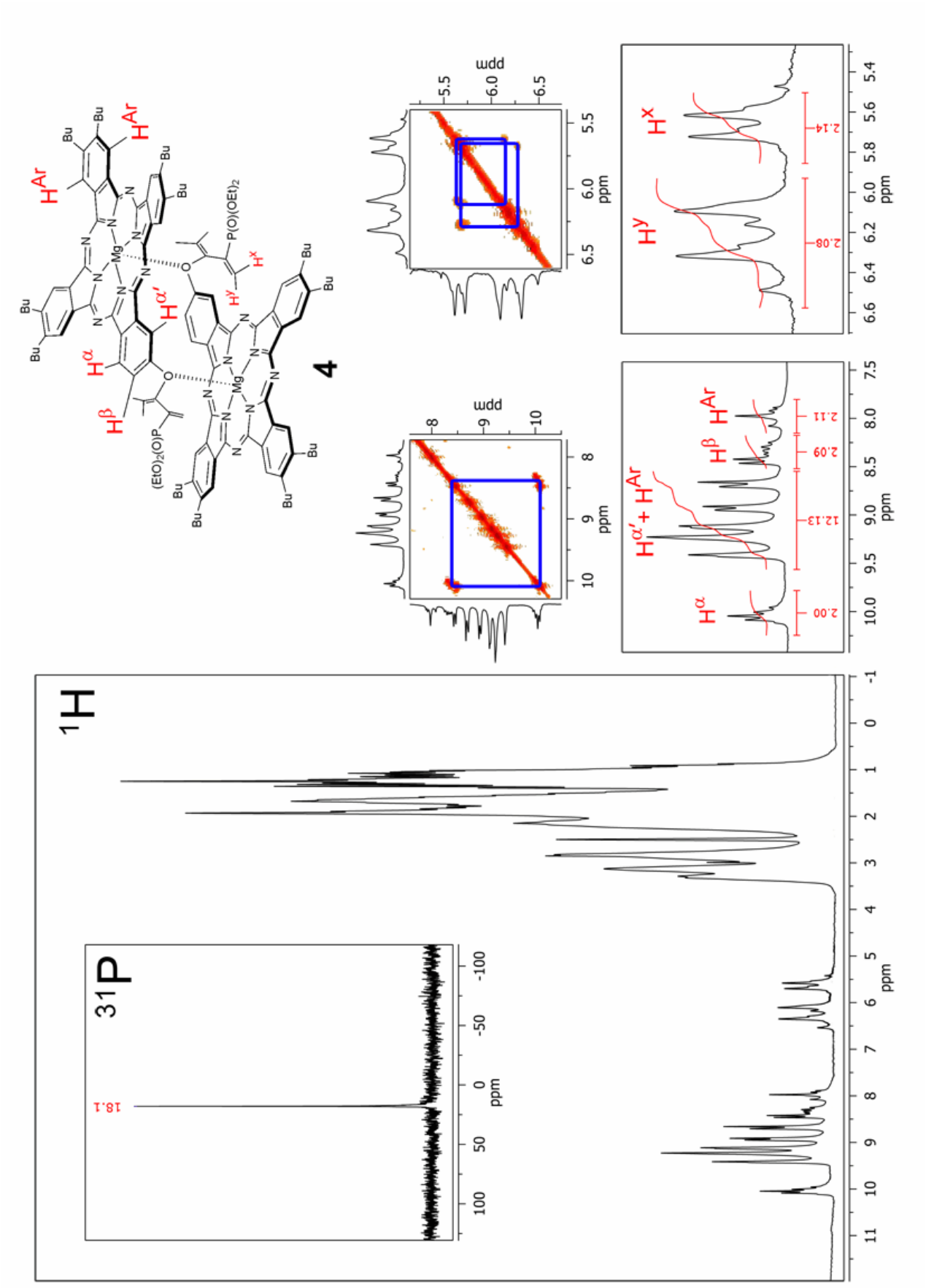

Fig. S3. ^{31}P, ^{1}H and ^{1}H–^{1}H COSY NMR spectra (CCl_4+5%DMSO-d_6) of **4**.

3. Infrared spectra

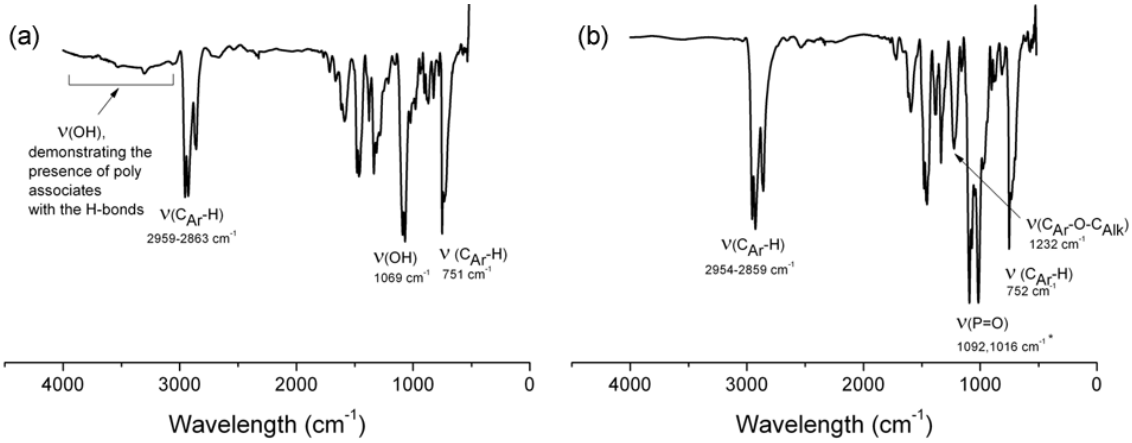

Fig. S4. FT–IR spectra of complexes **2** (a) and **4** (b) in CCl_4.

4. Fluorescence study

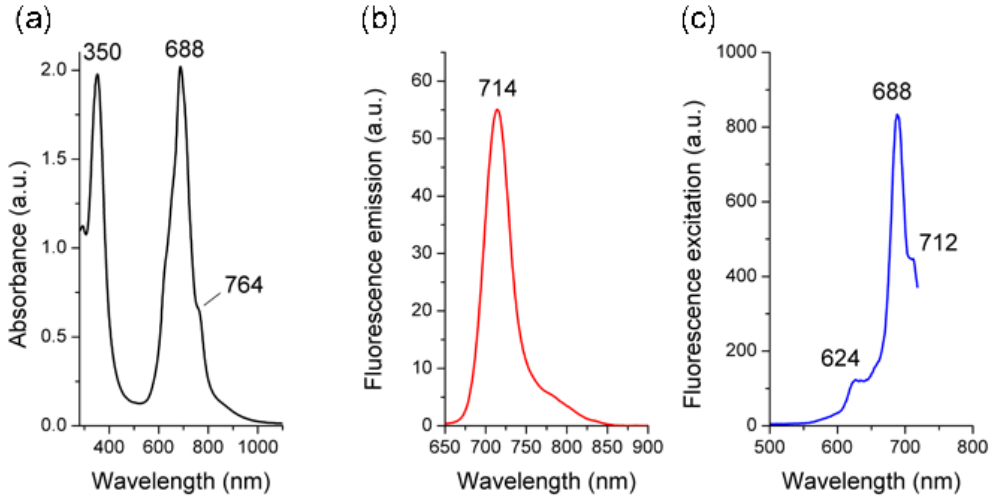

Fig. S5. UV–Vis (a, C=9.6×10^{-5} mol dm^{-3}), fluorescence emission (b, λ_{exc}=600 nm) and excitation (c, λ_{em}=730 nm) spectra (C=4.8×10^{-6} mol dm^{-3}) of **2** in toluene.

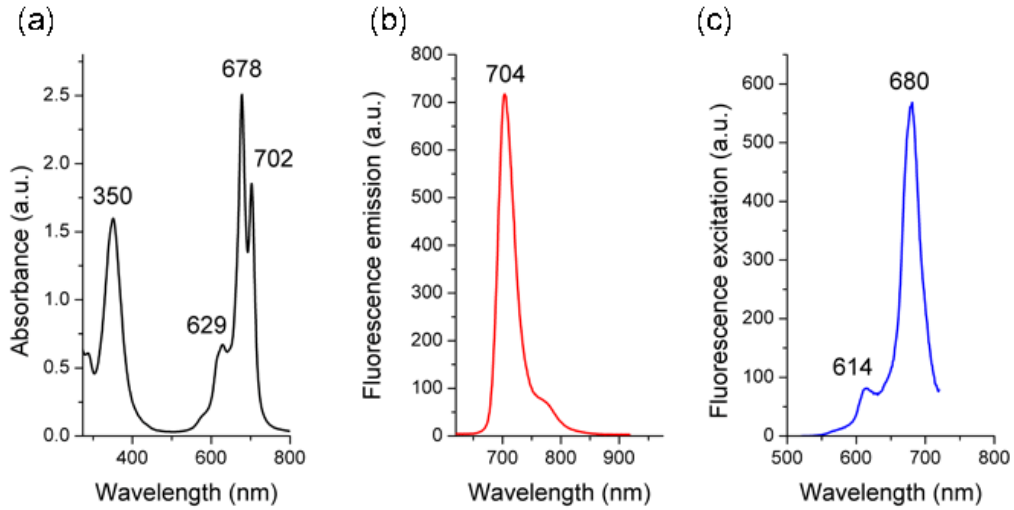

Fig. S6. UV–Vis (a, C=6.1×10^{-5} mol dm^{-3}), fluorescence emission (b, λ_{exc}=600 nm) and excitation (c, λ_{em}=730 nm) spectra (C=4.8×10^{-6} mol dm^{-3}) of **2** in THF.

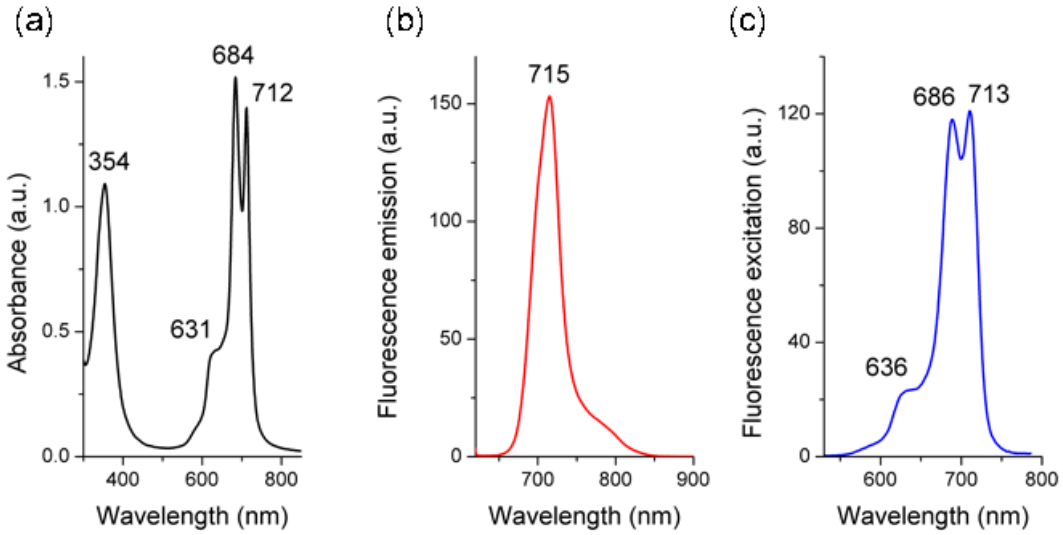

Fig. S7. UV–Vis (a, C=4.1×10^{-5} mol dm^{-3}), fluorescence emission (b, λ_{exc}=600 nm) and excitation (c, λ_{em}=800 nm) spectra (C=2.8×10^{-6} mol dm^{-3}) of **4** in toluene.

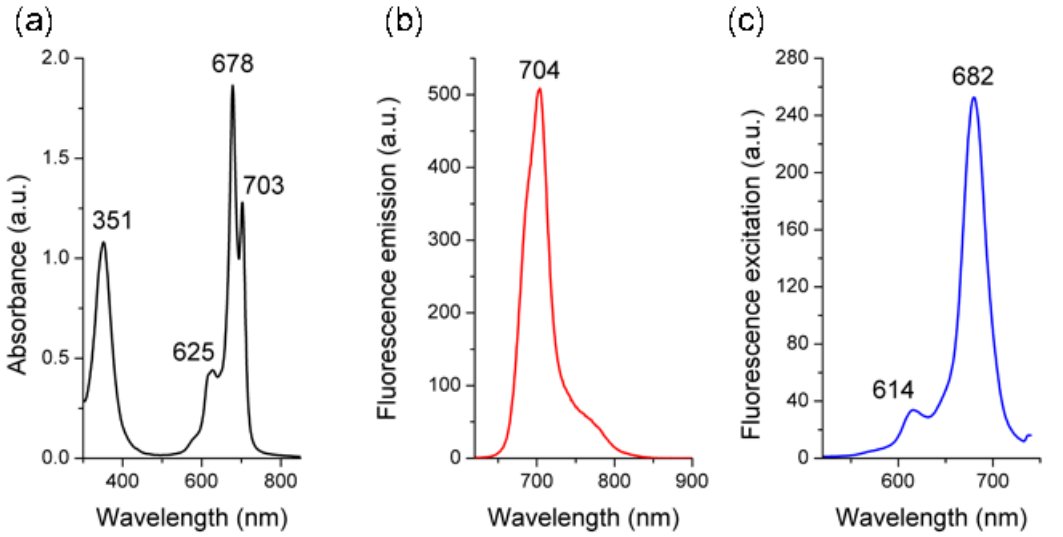

Fig. S8. UV–Vis (a, C=4.6×10^{-5} mol dm^{-3}), fluorescence emission (b, λ_{exc}=600 nm) and excitation (c, λ_{em}=730 nm) spectra (C=2.3×10^{-6} mol dm^{-3}) of **4** in THF.

5. DFT calculations

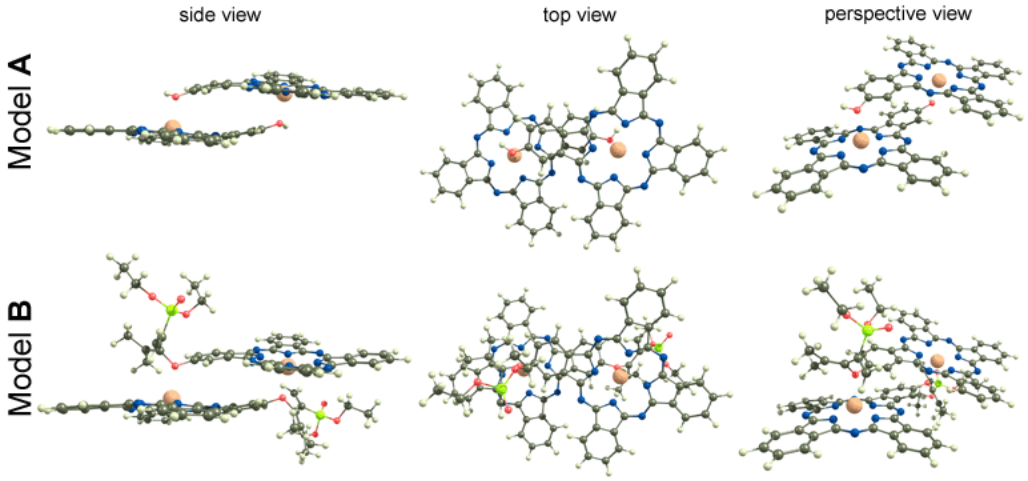

Fig S9. DFT-optimized structures for models based on compounds **2** and **4** with butyl groups replaced by hydrogen atoms for clarity.

Table S1. Appropriate computed data for models based on dimeric complexes **2** and **4**.

Property	Model	
	A	B
Total Energy, a.u.	–3884.0197	–5801.6064
Symmetry point group	C_2	C_2
The distance between Mg and O atoms, Å	2.25	2.25
The displacement of Mg outside the $4N_{iso}$ plane, Å	0.42	0.62
The distance between the centroid of one macrocycle and $4N_{iso}$ plane of the second one, Å	3.82	3.64
The distance between the macrocycles in the effective contact area, Å	2.59	2.77
The angle between the $4N_{iso}$ planes of the macrocycles, deg.	16.7	23.8
The distortion of isoindoline fragment in the effective contact area, deg.	15.67	9.84
The rotation angle of the macrocycles, deg.	30.5	35.8

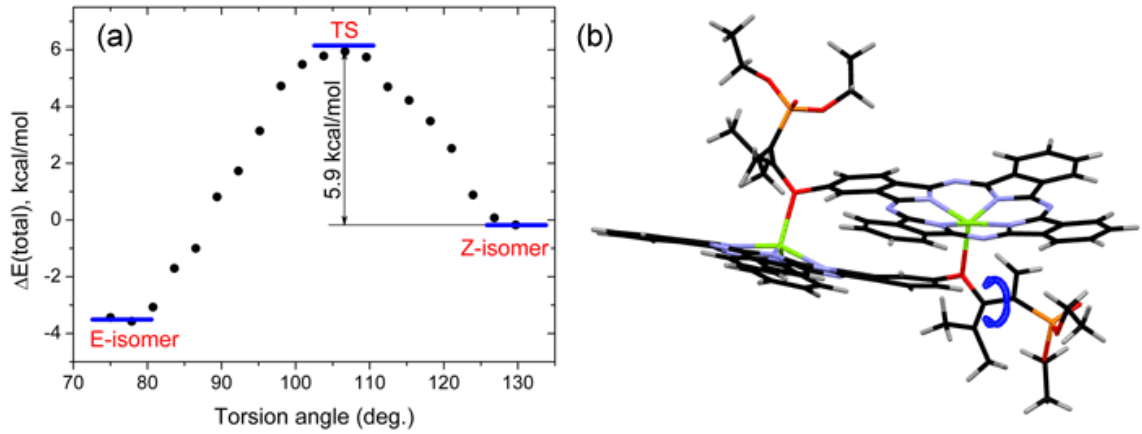

Fig S10. Scanning the PES of rotation of double bonds within the diene fragments on the periphery (a). For clarity, the single rotation is shown (b). The torsion angles Me_2**C**=**C**(OPc_2)–**C**(P(O)($OEt)_2$)=**C**H_2 were changing from 75° to 130° with a step of 3°.

In this work, DFT calculations were provided with quantum-chemical program PRIRODA [1]. PBE functional [2] and cc-pVDZ basis set [3] were used for optimization of the structure geometries corresponded to steady state as well as for scanning of the potential energy surface (PES). Butyl substituents were replaced with hydrogen atoms for reducing a calculation time. The size of the basis set used is {6s2p}/[2s1p] for H; {10s7p3d}/[3s2p1d] for C,N,O; {14s11p6d}/[5s4p2d] for Mg and {14s11p3d}/[4s3p1d] for P atoms respectively. The geometry coordinates and analytic gradients of optimized structures for the models based on dimeric complexes **2** and **4** are represented in Appendixes A and B.

5. TDHF calculations

Time-dependent Hartree Fock (TDHF) calculations were performed on the models of compounds **2** and **4** with GAMESS US package [4]. We suggest that butyl groups do not influence on comparison of NLO properties of the dimeric complexes, therefore they were replaced with hydrogen atoms to reduce a calculation time. The structures of Models **A** and **B** were initially optimized on HF/6-311++G** level of theory in order to obtain the most truthful results. In this work, static polarizabilities and zero-frequency first hyperpolarizabilities were calculated for prediction of NLO properties of dimers **2** and **4** and for making their comparison. The Tables below summarize data about the polarizability (α) and the first hyperpolarizability (β) tensor components.

Table S2. The static polarizability (α) tensor components (a.u.).

Model	α_{xx}	α_{yy}	α_{zz}	α
A	1596.8956	2007.9736	275.5811	860.1020
B	1716.9442	2285.7806	550.9043	970.4630

Table S3. The zero-frequency first hyperpolarizability (β) tensor components (a.u.).

Parameter	Model **A**	Model **B**
β_{xxx}	-1862.1508	2414.1149
β_{xyy}	-2510.1019	1681.2556
β_{xzz}	-130.0636	386.7217
β_{yyy}	351.2593	4369.3951
β_{yzz}	697.0069	455.4402
β_{yxx}	-368.4831	536.9856
β_{zzz}	-31.1741	80.3877
β_{zxx}	-508.5411	577.2290
β_{zyy}	-140.3314	317.9062
β	4603.8484	7056.1972

6. References

1. D. N. Laikov, Yu. A. Ustynyuk, *Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 820-826.
2. M. Erznzerhof, G.E. Scuseria, *J. Chem. Phys.*, 1999, **110**, 5029.
3. D.N. Laikov, *Chem. Phys. Lett.*, 2005, **416**, 116-120.
4. M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M.Dupuis, J.A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347–1363.

Table S4. Cartesian matrix for the model based on dimer **2** (optimized structure).

Atom No	x	y	z
6	5.94337417	2.16503135	1.94089382
6	6.23925115	3.51701076	1.68656389
6	5.22801274	4.43446401	1.39387399
6	3.91427207	3.96761894	1.35725771
6	3.61728009	2.60937524	1.61563177
6	4.62850612	1.69539736	1.91185232
6	2.63575591	4.63207358	1.09145539
7	1.63308996	3.69791509	1.17670855
6	2.16341467	2.47369182	1.50578706
6	-1.01823945	-2.37975045	1.54525973
6	-0.05952018	-1.37865782	1.66912568
6	-0.52475244	-0.06735787	1.74070794
6	-1.90672991	0.22825911	1.72635118
6	-2.85173142	-0.79717293	1.68565718
6	-2.39752238	-2.11164383	1.58406803
6	0.17960977	1.21489674	1.67715501
7	-0.75448285	2.21610123	1.57458297
6	-2.01975736	1.68375956	1.62697965
6	-4.56952116	4.37040099	1.40686627
6	-4.27102557	5.72896913	1.15037752
6	-5.27756644	6.69493913	1.13561505
6	-6.58786426	6.27705686	1.37489104
6	-6.88505089	4.92521443	1.63004199
6	-5.87932713	3.95736791	1.65290640
6	-3.29698470	3.64751254	1.36104180
7	-2.29576703	4.54453684	1.06939700
6	-2.82222052	5.80792153	0.95165794
6	2.20381117	9.03834916	0.43575903
6	1.75351472	10.35220491	0.29353410
6	0.37864217	10.65007657	0.25942872
6	-0.58096567	9.64162468	0.36646083
6	-0.13388959	8.32700473	0.49899751
6	1.24743126	8.02782297	0.53352924
6	-0.84045043	7.05243778	0.64563267
7	0.08998763	6.04445052	0.73157741
6	1.35721398	6.57674898	0.70046077
7	2.51882711	5.93813236	0.84575141
7	-2.16833567	6.94935467	0.72456438
7	1.50773547	1.32695930	1.68648516
7	-3.18267716	2.33466852	1.56584768
12	-0.33253093	4.05379987	0.78746174
8	-0.54868982	-3.67793983	1.27588619
1	6.75807452	1.47249798	2.16741835
1	7.27917246	3.85170352	1.72089846
1	5.44629760	5.48657769	1.19780531
1	4.38970190	0.64792020	2.10834221
1	1.00854997	-1.60626328	1.64248877
1	-3.91970181	-0.56943773	1.67735186
1	-3.11294576	-2.93355801	1.47905531
1	-5.03506783	7.74255304	0.94352152
1	-7.39898041	7.00961946	1.36800694
1	-7.92161370	4.63268688	1.81593335
1	-6.09838406	2.90685355	1.85686597
1	3.26840003	8.79657005	0.47078582
1	2.47810118	11.16618372	0.20983006
1	0.06046676	11.69000986	0.15023636
1	-1.65050071	9.86282572	0.34928868
1	-1.25217789	-4.32246509	1.49626340

6	6.40710358	-1.61032841	-0.36035769
6	6.74764763	-2.93372369	-0.02460835
6	5.78033761	-3.94008335	0.01481207
6	4.46366633	-3.59142592	-0.28522189
6	4.12251433	-2.26184040	-0.62521805
6	5.09100678	-1.25891404	-0.66803061
6	3.22314685	-4.36903376	-0.34184006
7	2.19572586	-3.52605815	-0.68689096
6	2.68160435	-2.25617885	-0.88585370
6	-0.80320111	2.29797666	-1.77822834
6	0.24030015	1.38678069	-1.64595012
6	-0.07452000	0.04045723	-1.81734193
6	-1.38414770	-0.37601319	-2.14732787
6	-2.39568309	0.56157273	-2.35690435
6	-2.09930077	1.90974334	-2.15929446
6	0.70150077	-1.17532808	-1.56436469
7	-0.13636103	-2.25609270	-1.68848666
6	-1.38972206	-1.83683405	-2.06309825
6	-3.66581081	-4.74016290	-2.46049441
6	-3.32269504	-6.06993056	-2.12199440
6	-4.21139547	-7.12101551	-2.34973186
6	-5.45112810	-6.81763234	-2.91522200
6	-5.79270564	-5.49446386	-3.25203033
6	-4.90291714	-4.44147927	-3.03234873
6	-2.51448507	-3.90843067	-2.10453960
7	-1.54357491	-4.71690218	-1.56061700
6	-1.96917066	-6.02305280	-1.56473970
6	3.03067864	-8.80339498	0.23362810
6	2.67680172	-10.15337582	0.27280304
6	1.36928099	-10.57169060	-0.03633437
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7	-1.29528560	-7.10488745	-1.16786027
7	1.99389685	-1.16975839	-1.23843950
7	-2.46863964	-2.58838716	-2.28878285
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1	7.78815160	-3.17495407	0.20733124
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1	-2.88776022	2.66413080	-2.24666137
1	-3.93350684	-8.14526430	-2.09109645
1	-6.17008544	-7.61889804	-3.10410874
1	-6.77094066	-5.29240360	-3.69567269
1	-5.15550261	-3.41213103	-3.29661553
1	4.04430054	-8.46829731	0.46452600
1	3.42599263	-10.90119135	0.54497638
1	1.12689035	-11.63680670	0.00100494
1	-0.63345492	-9.96546630	-0.64196684
1	-1.21242853	4.21178558	-1.81132263

Table S5. Cartesian matrix for the model based on dimer **4** (optimized structure).

Atom No	x	y	z
6	6.28343658	2.29070466	1.20019599
6	6.49471605	3.66367273	0.97326494
6	5.42166364	4.53978851	0.79918411
6	4.13256601	4.00827917	0.84383311
6	3.92138020	2.62989467	1.06879112
6	4.99401833	1.75797791	1.25741245
6	2.80639528	4.61891550	0.73266878
7	1.85300766	3.63410836	0.84102898
6	2.47175700	2.42800114	1.07872835
6	-0.43455145	-2.58680480	1.47665956
6	0.48103693	-1.54052586	1.46986924
6	-0.03665918	-0.24987671	1.58041310
6	-1.42211093	-0.02438547	1.72906525
6	-2.31684416	-1.09373943	1.80574880
6	-1.81140908	-2.38544178	1.66814935
6	0.58701646	1.06582779	1.42831576
7	-0.39850695	2.02225079	1.43604192
6	-1.61414331	1.42559881	1.66698438
6	-4.24404582	3.99578028	2.08664027
6	-4.02383684	5.38357194	1.94118189
6	-5.04407495	6.30327017	2.18425364
6	-6.29074157	5.80717465	2.56987249
6	-6.50996962	4.42468488	2.71671904
6	-5.48822826	3.50293492	2.48108138
6	-2.97462424	3.33906743	1.76929816
7	-2.05256453	4.29793009	1.42379245
6	-2.62649089	5.54229618	1.53407557
6	2.17225626	9.03455533	0.75959289
6	1.67734142	10.33065766	0.91737428
6	0.30684582	10.56361542	1.14189731
6	-0.60217344	9.50641242	1.21520722
6	-0.11144244	8.21138032	1.04426605
6	1.26305782	7.97757172	0.81707764
6	-0.75798197	6.89777509	1.07273786
7	0.19159219	5.93200527	0.83150073
6	1.42666902	6.52564635	0.71861602
7	2.61745221	5.93417447	0.62672372
7	-2.04837086	6.72921404	1.35528204
7	1.89961165	1.24479304	1.29607699
7	-2.79689302	2.01865031	1.82829999
12	-0.18056414	3.91760142	0.64502595
8	0.02092249	-3.89577007	1.16172976
1	7.14495324	1.63279593	1.34042221
1	7.51734181	4.04810570	0.93982708
1	5.57365291	5.60898629	0.63543411
1	4.81949557	0.69591041	1.44236442
1	1.54867812	-1.71420847	1.32516722
1	-3.38803660	-0.91415026	1.92058844
1	-2.47717050	-3.25052781	1.67715909
1	-4.86158973	7.37395240	2.06975827
1	-7.11272091	6.50121511	2.76257598
1	-7.49820664	4.07070971	3.02119626
1	-5.64630358	2.42832000	2.59638918
1	3.23501472	8.84099501	0.59737593
1	2.36283784	11.18089549	0.87260276
1	-0.04658508	11.59044184	1.26589135
1	-1.66554926	9.67407747	1.40027064
6	6.71145055	-1.48097332	-0.94925497
6	7.13780244	-2.80101574	-0.71198365
6	6.22259907	-3.85330355	-0.64333091

6	4.87025570	-3.55313118	-0.80804113
6	4.44266617	-2.22757265	-1.04598649
6	5.35937650	-1.17903299	-1.12439173
6	3.66514300	-4.38492053	-0.81307505
7	2.57140248	-3.58064733	-1.01878403
6	2.98659308	-2.28056497	-1.18707769
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6	-3.58171690	-7.42160316	-2.95829892
6	-4.83129157	-7.15560167	-3.52127922
6	-5.25928658	-5.83457938	-3.75054517
6	-4.44819194	-4.74641581	-3.42311773
6	-2.11580399	-4.13711113	-2.40425562
7	-1.10044494	-4.91667083	-1.90147525
6	-1.43485530	-6.24231550	-2.03584821
6	3.75199827	-8.84999249	-0.56800893
6	3.48079402	-10.21747225	-0.64334075
6	2.19188624	-10.68698370	-0.95808962
6	1.14187592	-9.80062159	-1.20522244
6	1.40697415	-8.43386970	-1.11594380
6	2.70104327	-7.96258664	-0.80019529
6	0.57235732	-7.24857038	-1.32334829
7	1.33265604	-6.12692036	-1.09436895
6	2.62726557	-6.50018650	-0.82341435
7	3.69186278	-5.71183018	-0.67023351
7	-0.69503226	-7.30978533	-1.73256922
7	2.23304850	-1.21065777	-1.43957637
7	-2.15269814	-2.80904786	-2.51037973
12	0.60872534	-4.20813711	-0.98893371
8	-0.53626308	3.51723211	-1.59888057
1	7.45358719	-0.68013456	-1.00070958
1	8.20425610	-3.00281730	-0.58330518
1	6.54334563	-4.88271014	-0.46843736
1	5.01991964	-0.15816983	-1.31234482
1	1.32754469	1.62166644	-1.42071884
1	-3.18686658	-0.01685738	-2.91125294
1	-2.75467593	2.43140422	-2.62075522
1	-3.23587581	-8.44304642	-2.78440559
1	-5.48972316	-7.98456475	-3.79315952
1	-6.24259243	-5.66195947	-4.19541770
1	-4.76689487	-3.71741561	-3.60390759
1	4.75143550	-8.47485004	-0.33653708
1	4.28149733	-10.93863529	-0.46050538
1	2.01528240	-11.76416180	-1.01427629
1	0.14091147	-10.15391740	-1.46324215
6	-0.71330543	4.45487400	-2.69726034
6	0.33262928	4.54357409	-3.56039489
6	1.65010035	3.87283980	-3.26743895
6	0.30921470	5.23961745	-4.89092068
6	-1.98683525	5.18898644	-2.60743806
6	-2.95124270	4.84635608	-1.71989481
6	-3.90995222	5.78210344	-5.46558093
6	-0.56640611	8.31171031	-2.50414638
6	0.35541725	9.42066185	-2.97195504
6	-4.02503605	5.86945042	-6.97588048

```
 1     1.18563726   9.01536582  -3.57019923
 1    -0.19417811  10.15492728  -3.57982128
 1    -1.41137361   8.71388960  -1.92166659
 1    -0.02341901   7.58205761  -1.88142006
 1     1.84270375   3.76889538  -2.19118000
 1     1.69692701   2.86724042  -3.72223263
 1     2.46208857   4.46719866  -3.71543002
 1    -0.68828291   5.52762239  -5.23393087
 1     0.94905670   6.13754775  -4.87293183
 1     0.74930239   4.55061078  -5.63407282
 1    -3.83144534   5.48297162  -1.61630147
 1    -2.87256984   3.97193570  -1.07329550
 1    -4.98106868   5.42535041  -7.29578790
 1    -3.99783369   6.91805976  -7.30757781
 1    -3.20607295   5.32168500  -7.46613259
 1    -3.94531224   4.73195018  -5.12514742
 1    -4.71848784   6.34066459  -4.96572450
 1     0.77607263   9.93079794  -2.09115479
 8    -3.60919266   7.41445894  -2.86287352
 8    -2.63074541   6.36310611  -5.08025792
 8    -1.08307621   7.62239187  -3.68578382
15    -2.43592097   6.75052478  -3.50327870
 6     0.21134989  -4.79687091   2.26933519
 6    -0.56870295  -5.88815629   2.36440329
 6    -1.73775503  -6.16560554   1.46275048
 6    -0.30169517  -6.95373135   3.39229134
 6     1.34491326  -4.41036633   3.15547175
 6     2.62884329  -4.51438593   2.77373663
 6     1.65171560  -5.66842395   6.48489753
 6    -0.67151096  -1.80080919   5.49506594
 6    -1.51318284  -2.26289037   6.67271000
 6     0.99947466  -6.46140614   7.60292753
 1    -2.43196242  -2.75986120   6.32693464
 1    -0.95137128  -2.96383214   7.30784666
 1     0.25901702  -1.31232575   5.82789655
 1    -1.22661023  -1.10192949   4.85167698
 1    -1.92252443  -5.36388736   0.73741019
 1    -1.57572703  -7.10238335   0.90253500
 1    -2.64669504  -6.31201642   2.07285671
 1     0.58015089  -6.73876401   4.00532747
 1    -1.17119988  -7.06921566   4.06164180
 1    -0.15261698  -7.92189535   2.88243912
 1     3.42560357  -4.14715639   3.42723291
 1     2.91314051  -4.95032844   1.81064600
 1     1.76544341  -7.05283696   8.12949209
 1     0.51881811  -5.78880757   8.32930568
 1     0.23951657  -7.15109209   7.20537537
 1     2.15346082  -6.34442665   5.76754213
 1     2.40173170  -4.95985255   6.87263856
 1    -1.79698953  -1.38860090   7.28135802
 8     2.24937043  -2.91449737   5.34531461
 8     0.61100337  -4.92345684   5.79256008
 8    -0.33018576  -2.91815517   4.61696735
15     1.08058243  -3.68184865   4.81936171
```

Table S6. Analytic gradient matrix for the model based on dimer **2** as a part of OUT file.

```
$Energy
 E=-3.884019678279e+03
 D=-9.15919660e-01 -4.10820279e-02 -1.16999778e-01
 G= 6.02300124e-07  9.83907744e-07  1.63702713e-06
    2.42692840e-07 -1.05771259e-06 -2.28411846e-06
    7.61301408e-07 -2.89764902e-06 -9.58543902e-06
    3.21457826e-06  3.46727041e-06  5.68045444e-06
   -1.01022911e-06 -1.59072020e-06  8.77767877e-06
   -2.38242787e-06  3.50340550e-06  6.69634357e-06
   -5.92177270e-06 -3.40129612e-06 -2.79273059e-06
    4.82738957e-06 -1.54000520e-06 -1.00363449e-05
   -6.82392445e-07 -5.39853146e-06 -9.94178364e-08
   -4.26261228e-06  1.18857166e-05 -8.16789367e-06
    2.11670842e-06  9.86484995e-06  9.06098107e-06
    6.07976449e-06  4.26716202e-07 -1.47870626e-05
   -6.54743520e-06 -4.03789026e-06 -1.32935630e-05
    4.01740303e-06  5.12928201e-06  2.16965822e-05
    2.89169979e-06 -9.78393861e-06 -3.67895916e-06
   -3.77547567e-06 -2.50518736e-06  5.77368478e-06
    5.90362767e-06 -4.62066182e-06 -1.47217395e-05
   -3.09994794e-06  2.87151275e-06  1.12716094e-05
   -3.81025538e-07 -1.99350339e-09  1.07006458e-05
    3.24595570e-06  2.74032709e-06  2.85493866e-06
   -9.33029328e-07 -1.47185793e-06 -5.73889751e-06
   -2.35247818e-07 -2.15732405e-08 -2.29629037e-06
   -3.43789333e-07  3.33988663e-07  9.20283130e-07
    1.21051001e-06  1.44223339e-06  1.64343971e-06
   -4.30875070e-06 -1.09610858e-05 -1.21060240e-05
    4.25108304e-06  1.50805471e-05 -5.99826098e-06
   -5.49042950e-06 -7.35119543e-06  6.53591678e-06
   -7.22765667e-07 -9.94514790e-07 -6.77196453e-07
   -1.01659776e-06  1.09930868e-06  1.36006849e-08
    1.42216056e-06  5.53352376e-07 -8.95421715e-07
   -9.04208871e-08 -2.32228110e-06 -4.85291332e-06
    1.16647332e-06  2.75504924e-06  5.90724648e-06
    1.62036360e-06  4.30084681e-06  9.06715995e-06
   -4.21713321e-06 -3.98438809e-06 -1.00445431e-05
    6.14446146e-08  8.42465019e-06  1.97484745e-05
   -6.23702890e-06 -8.89283382e-06 -2.45029504e-05
    2.39188353e-06  3.04094145e-06  9.61292239e-06
    3.76045790e-06  4.25941872e-06 -7.05945420e-06
    2.15532337e-06  5.62950709e-06  4.76902716e-06
    3.38407320e-06  4.94840073e-06  2.80888556e-06
    5.88590843e-06 -7.20699602e-06  1.06285165e-05
   -8.32288106e-06 -6.37962836e-06 -3.25602976e-06
    1.54395349e-07 -6.46205011e-07 -3.63425535e-06
   -3.46786329e-07  8.44875498e-07  3.40396075e-06
   -4.38682757e-07  5.87766254e-07  1.52053363e-06
    7.66382464e-08 -8.91912144e-07 -2.29943793e-06
   -1.58056009e-06 -8.28119162e-06  4.86430943e-07
   -1.75110155e-07  6.24389483e-07 -8.37625943e-06
   -8.45552808e-07  1.40502315e-06  2.01350561e-06
    2.02699670e-07  3.69254820e-07  1.76104196e-06
    2.49876202e-07  2.87703243e-07  2.01716429e-06
   -3.55715312e-07 -2.83691462e-07 -2.65510626e-06
    3.64402273e-07 -8.17715338e-07 -1.40824074e-06
   -4.00331615e-08 -1.85438566e-07 -2.37748642e-07
   -5.19047059e-08 -6.09294412e-08 -1.35072359e-06
   -1.66499275e-07 -9.29126558e-08 -6.51991972e-07
```

```
    1.67239643e-08  3.15732409e-07  1.64400768e-06
    2.80795255e-06 -2.04492468e-06  4.26195828e-06
    9.87250696e-07 -1.11430272e-06 -1.35697660e-06
   -3.45708453e-07  9.63488433e-07  2.37042205e-06
   -1.93773442e-06  2.74903529e-06  9.07456628e-06
    4.44464620e-06 -3.46182334e-06 -5.20587989e-06
    1.00842407e-07  1.53099678e-06 -7.21645505e-06
    3.64629111e-07 -2.29471998e-06 -7.30108746e-06
   -6.22388918e-06  3.34500312e-06 -1.72242102e-06
    2.05516365e-06  3.11333721e-06  1.18000981e-05
   -6.42683233e-07  5.61724345e-06  2.34163236e-06
   -3.67246735e-06 -1.14684554e-05  7.65841947e-06
    3.59696568e-06 -7.58128790e-06 -7.68545112e-06
    3.73861313e-06 -7.49343629e-07  1.40467475e-05
   -1.15850252e-05  1.17912455e-06  6.44753789e-06
    1.01704909e-05 -3.81648312e-06 -1.88474867e-05
    9.42951582e-07  9.27388105e-06  3.66767245e-06
   -1.34283727e-06  6.11811940e-06  3.93221935e-07
   -4.17895218e-06  3.17717310e-06  9.04864954e-06
    8.84404354e-06 -1.50557313e-06 -7.01605947e-06
    2.20107033e-06 -1.41790348e-06 -8.79630807e-06
    3.28744388e-06 -1.67159555e-06 -5.01915589e-06
   -2.54450340e-06  7.88425566e-07  4.99415104e-06
   -5.56982424e-07  2.39058986e-08  1.68514931e-06
   -6.76733470e-09 -5.43281298e-07 -9.80103343e-07
    6.50697677e-07 -4.86501294e-07 -1.84985763e-08
   -4.18833802e-06  1.30487182e-05  7.14508776e-06
    3.85796154e-06 -1.61988998e-05  5.18508438e-06
   -4.10061888e-06  7.28593075e-06 -2.56823217e-06
   -1.08100439e-06  9.94319425e-07  9.88843298e-07
   -8.03642591e-07 -1.29074059e-06 -4.13426437e-07
    1.43455997e-06 -3.88815831e-07  1.38845132e-06
   -1.28823885e-06  2.35061537e-06  3.95764448e-06
    2.32727941e-06 -2.01812069e-06 -5.42416182e-06
    4.42773946e-06 -4.34332762e-06 -9.05239048e-06
   -7.65872700e-06  3.25170343e-06  1.23155553e-05
    6.61625675e-06 -5.67514768e-06 -1.88482926e-05
   -1.07346581e-05  7.40747109e-06  1.90898355e-05
    3.43396675e-06 -3.25109217e-06 -3.88105460e-06
    3.14569859e-06 -3.48858121e-06  2.90228955e-06
    3.22455458e-06 -7.01131213e-06 -9.29562388e-06
   -2.33687345e-06 -6.40569240e-06  6.04798103e-07
    6.57435382e-06  4.35010386e-06 -7.34455165e-06
   -1.16122364e-05  3.70516024e-06  1.89461491e-06
   -7.30368699e-07  6.13299678e-07  3.20551660e-06
    5.20124334e-07 -7.73346688e-07 -2.92294371e-06
    2.48168002e-07 -5.72872600e-07 -1.70291775e-06
   -5.09824730e-07  5.30408365e-07  2.27628485e-06
   -2.15473228e-06  6.48611865e-06 -4.77942718e-07
   -2.48137794e-06 -4.87867957e-07  8.62064189e-06
   -3.67929950e-07 -1.53416970e-06 -2.03058192e-06
    7.65967330e-07 -1.23390495e-07 -1.03516902e-06
    6.12757800e-07 -1.94156482e-07 -1.46405107e-06
   -9.45165661e-07  2.97573348e-07  2.40525085e-06
    1.40339658e-07  1.46646148e-07  7.63007306e-07
   -9.20019636e-08  3.03567071e-07  1.59802165e-07
   -3.74770803e-07  7.26271188e-08  1.36879498e-06
   -3.43995690e-07  9.64810273e-08  5.34588075e-07
    5.42612641e-07 -4.84478431e-07 -1.47419875e-06
    4.48135295e-06  4.08369033e-06 -4.65794519e-06
$end

 G(max) = 0.00002450
```

Table S7. Analytic gradient matrix for the model based on dimer **4** as a part of OUT file.

```
$Energy
 E=-5.801606423596e+03
 D=-4.08015383e-01 -9.28632875e-01  8.13645870e-02
 G= 2.05226868e-07 -5.33233854e-07  4.70358227e-08
    1.11994088e-07 -4.76671992e-07 -2.71182760e-07
    2.09806963e-07 -1.73256252e-07 -1.16348788e-08
    5.57328121e-07 -4.53263119e-07 -1.46856365e-06
    1.57977827e-06 -9.56725268e-07 -3.12308626e-06
   -1.03744856e-08  5.21425097e-07  1.58107656e-06
   -5.07917054e-07  9.60786556e-07  7.17445705e-08
    1.89624043e-06  4.05945264e-07 -4.88982416e-06
   -3.80552542e-06  2.55139916e-06  6.52652339e-06
    1.34870771e-07 -5.08215588e-07 -6.12773058e-06
   -4.06300526e-06  2.59486648e-06 -1.08322039e-05
    8.51263493e-07 -1.09404862e-07  1.07779789e-05
    9.01540065e-07 -1.55956054e-06  1.81743111e-07
   -2.57797598e-06  1.23495398e-06 -5.00420187e-06
    2.21012753e-06  6.16710153e-07  4.32857336e-06
   -1.79135512e-06  3.60833172e-07 -1.18495730e-05
   -3.04888809e-06 -4.35726998e-06 -5.61518106e-06
    1.58902782e-06  3.43476736e-06  3.42994871e-06
   -4.94675388e-07  2.29259972e-07  7.75545654e-07
   -1.68016488e-07 -1.89290975e-07  2.31945142e-07
    1.51778876e-06  2.08191864e-07 -1.16886669e-07
    1.70888944e-07  7.36188237e-07 -6.84918035e-08
    1.30589161e-07  4.78233286e-08  3.56077371e-07
    1.66813516e-06 -1.61743253e-07  9.42230248e-07
    2.02948959e-07  2.07366984e-06 -2.78835394e-06
   -5.67750818e-07 -3.55702105e-06  6.30419290e-07
   -4.54938326e-07  2.71030747e-06 -2.16906353e-06
    2.06514279e-06  1.51957572e-06 -2.46406277e-06
   -1.15375354e-06 -2.10084759e-06  3.29853879e-06
    1.13891783e-06  2.21075786e-06 -9.72159693e-07
   -1.02834026e-07 -1.32387697e-06 -2.70592949e-06
    6.70675501e-07 -7.43563954e-07  2.22797979e-06
    7.30923194e-07 -4.56580822e-07 -2.65541397e-07
   -1.59585250e-06  4.34557376e-06  2.50834630e-06
    2.81779691e-07 -1.17513004e-06 -7.14073757e-07
   -3.99214143e-06 -5.74045462e-07  2.30866460e-07
    2.60087026e-06 -1.62151948e-06  2.97092351e-06
    1.43986295e-06 -1.87058123e-06  8.34611192e-07
    2.84192269e-06 -1.64753907e-06  1.26591477e-06
    5.93288775e-07 -1.06677204e-06  4.71923096e-06
    4.24848671e-06  4.14558652e-06  2.65230018e-06
    1.11732276e-05  6.83823660e-06  1.13523022e-06
    2.22090200e-07 -2.14479608e-07 -8.96161039e-07
    1.88277941e-07 -1.69029466e-07  6.99941978e-09
    2.80302591e-07 -1.92364155e-07 -1.55403100e-07
   -2.68434446e-07 -7.04549742e-08  4.89290379e-07
    9.70562130e-07 -1.56863459e-06  6.31957256e-06
    3.20367768e-07 -1.05657464e-06  1.81877344e-06
   -1.47431948e-06  5.14121502e-07 -1.26034687e-06
    1.90352511e-08  3.60617622e-07  5.73911798e-07
    1.42306362e-07 -1.75181814e-07  3.81752418e-07
    4.95504685e-08  5.80831568e-07  3.18749765e-08
   -1.65346977e-07  1.84581342e-07  2.83426358e-07
   -6.98582067e-10 -3.46571075e-07 -5.28215689e-07
    4.42403888e-07  1.88780742e-07 -5.17530793e-07
    5.80760918e-07 -3.32818158e-07 -3.91212209e-07
    3.54320206e-07 -5.63110251e-09  1.24243534e-06
   -4.56295906e-07 -4.99896974e-08  6.87850418e-07
    2.59662835e-08  1.58300410e-08 -1.43521841e-06
```

```
-5.44701472e-07 -1.28376269e-06 -1.23899599e-07
 1.16237454e-07  9.85845145e-07 -2.97768399e-08
 2.27487910e-07 -7.16732183e-07  1.79093345e-06
 4.43305739e-07 -3.96191715e-07 -3.22943400e-06
 2.53259114e-06  1.76241481e-07  1.08666205e-06
 2.67224591e-06 -3.78749388e-06 -1.93421550e-06
-3.24143940e-06  3.21849325e-06  7.69590924e-06
 4.07235433e-07 -4.60747072e-06 -3.09541679e-06
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