Supporting Information for

Photoluminescent properties and molecular structures of dinuclear gold(I) complexes with bridged diphosphine ligands: near-unity phosphorescence from ^{3}XMMCT/^{3}MC

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Contents

1. General Information

^{1}H and ^{31}P NMR spectra were recorded on a Bruker AVANCE-400 spectrometer. ^{1}H chemical shifts were referenced to residual solvent peaks. ^{31}P chemical shifts were referenced to an external standard, 85% phosphoric acid (δ = 0 ppm). Elemental analyses (C and H) were carried out using an elemental analyser (Vario EL CHNOS) from Elementar. For the photo-physical studies, dissolved oxygen was removed by repeated freeze-pump-thaw cycles. Steady-state emission spectra were recorded at room temperature and at 77 K using a Hitachi F-7000 spectrofluorometer. The intensity distribution of the Xenon lamp incorporated in the spectrofluorometer was corrected using Rhodamine B in ethylene glycol. The output of the photomultiplier tube was calibrated between 300 and 850 nm with a secondary standard lamp.

Laser photolysis studies were performed using a Nd:YAG laser (Sure Light 400, Hoya Continuum Ltd.) equipped with second, third, and fourth harmonic generators. The laser pulses used for the emission lifetime measurements were of the third harmonic (355 nm). The duration and energy of the laser pulse were 10 ns and 30 mJ/pulse, respectively. The system used to monitor the emission decay was reported elsewhere.[S1]

An Optistat DN-V2 cryostat from Oxford Instruments was used to measure the emission spectra and lifetimes in the temperature range from 293 to 83 K. After the measurement of emission spectra and lifetimes at 83 K, that at 293 K was performed again to confirm that crystallization solvents have not been removed from the crystals. Crystalline powders of samples used for emission measurements were sealed in quartz tubes with a diameter of 3 mm. Optical measurements at 77 K were carried out at the temperature of liquid nitrogen using a Dewar vessel with four optical windows. After filling the vessel with liquid nitrogen, the sample, which was placed in a quartz tube with a diameter of 5 mm, was immersed into the liquid nitrogen for rapid cooling, and luminescence spectra and lifetimes were measured.

Emission quantum yields were determined at room temperature and at 77 K using an absolute PL quantum yield measurement system (C-9920-02G, Hamamatsu).[S2]

A suitable crystal for **1DOR**, **2DOR**, **3DOR**, and **3DGR** was selected and mounted using Paratone-N oil on a Cryo-Loop. X-ray Diffraction data was collected at 93 K under a cold nitrogen gas stream on a Rigaku XtaLAB Pro MM007HF X-ray diffractometer system, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data were collected by an ω-scan with 0.5° oscillations for each frame. Bragg spots were integrated using the CrysAlis^{Pro} program package.[S3] Structures were solved by SHELXT[S4] and refined by SHELXL.[S5] All non-disordered non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined by applying riding models. CCDC reference numbers are 2026816 for **1DOR**, 2026817 for **2DOR**,

2026818 for **3DOR**, and 2026819 for **3DGR**, respectively.

The lowest triplet excited (T_1) states were optimized by density functional theory (DFT) calculations at gas-phase conditions.[S6] The input coordinates were extracted from the X-ray crystallographic data. The crystalline solvents THF or acetone molecules were fixed (opt = modredundant) in structural optimization calculations. The UM06 level of theory[S7] were used for geometry optimizations using Gaussian 16, C. 01.[S8] The def2–TZVP basis set for Au atoms, def2–SV basis set for other atoms, were used.[S9] Time dependent (TD)-DFT calculations were performed on the optimized T_1 geometries: the M06 level of theory, def2-TZVP for Au and I atoms, and def2-SVP for other atoms were applied. All calculations were performed with tight criteria. Natural transition orbitals (NTOs) were generated by orbital transformation followed by a singular value decomposition of the transition density matrix. In the NTO representation, the electronic transitions can be expressed by one single "hole (approximately HOMO) - electron (approximately LUMO)" pair with an associated eigenvalue of essentially one, even for transitions that are highly mixed in the canonical MO basis. This procedure can be a helpful strategy for obtaining a simple orbital interpretation of "what got excited to where".[S10] Perturbative spin-orbit coupling calculations (pSOC-TD-DFT) were performed to understand singlet and triplet contributions to the excitations with the ADF2019.303 package[S11] on the previously optimized T_1 structures. The M06 level of theory, TZP for Au and I atoms, and DZP for other atoms were applied.

2. Crystal Structure determination

Table S1. Crystallographic data for 1DOR and 2DOR.

	1DOR	**2DOR**
formula	$C_{50}H_{64}Au_2Cl_2O_2P_2$	$C_{50}H_{64}Au_2Br_2O_2P_2$
formula weight	1223.80	1312.70
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
a / Å	13.9885(6)	14.0829(7)
b / Å	16.7416(7)	16.7889(7)
c / Å	20.1362(7)	20.2432(8)
α / deg	90	90
β / deg	90	90
γ / deg	90	90
V / Å^3	4715.7(3)	4786.2(4)
Z	4	4
d_{calcd} / g cm^{-3}	1.724	1.822
T / K	93(2)	93(2)
radiation	Mo Kα	Mo Kα
	(λ = 0.71073 Å)	(λ = 0.71073 Å)
μ / cm^{-1}	6.434	7.898
diffractometer	Rigaku XtaLAB Pro	Rigaku XtaLAB Pro
	MM007HF	MM007HF
max 2θ / deg	60	60
reflns collcd	33517	32230
indep reflns	14933	15027
	(*R*int = 0.0437)	(Rint = 0.0440)
no. of param refined	531	531
R1,[a] *wR2* ($I > 2\sigma I$)[b]	0.0291, 0.0602	0.0311, 0.0590
S	1.013	1.041

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR2 = [\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2]^{1/2}$

Table S2. Crystallographic data for **3DOR** and **3DGR**.

	3DOR	**3DGR**
formula	$C_{50}H_{64}Au_2I_2O_2P_2$	$C_{48}H_{60}Au_2I_2O_2P_2$
formula weight	1406.70	1378.64
cryst syst	orthorhmbic	orthorhmbic
space group	$P2_12_12_1$	$Pdd2$
a / Å	14.06858(18)	29.5244(5)
b / Å	17.0216(2)	28.5111(5)
c / Å	20.3878(2)	11.30808(18)
α / deg	90	90
β / deg	90	90
γ / deg	90	90
V / Å^3	4882.26(10)	9518.8(3)
Z	4	8
d_{calcd} / g cm^{-3}	1.914	1.924
T / K	93(2)	93(2)
radiation	Mo Kα	Mo Kα
	(λ = 0.71073 Å)	(λ = 0.71073 Å)
μ / cm^{-1}	7.370	7.558
diffractometer	Rigaku XtaLAB Pro	Rigaku XtaLAB Pro
	MM007HF	MM007HF
max 2θ / deg	60	60
reflns collcd	94419	61648
indep reflns	15766	7505
	(Rint = 0.0260)	(Rint = 0.0366)
no. of param refined	531	259
$R1$,[a] $wR2$ ($I > 2\sigma I$)[b]	0.0179, 0.0302	0.0134, 0.0287
S	1.041	1.034

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR2 = [\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2]^{1/2}$

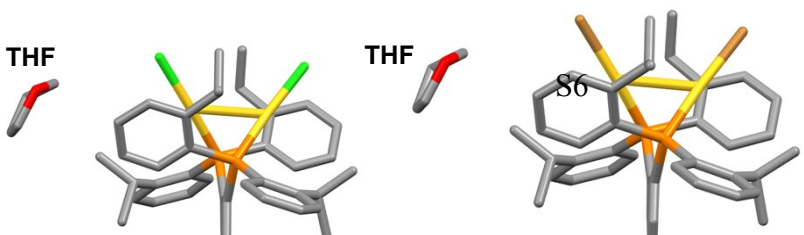


Fig. S1 Perspective views of **1DOR**, **2DOR**, **3DOR,** and **3DGR**.

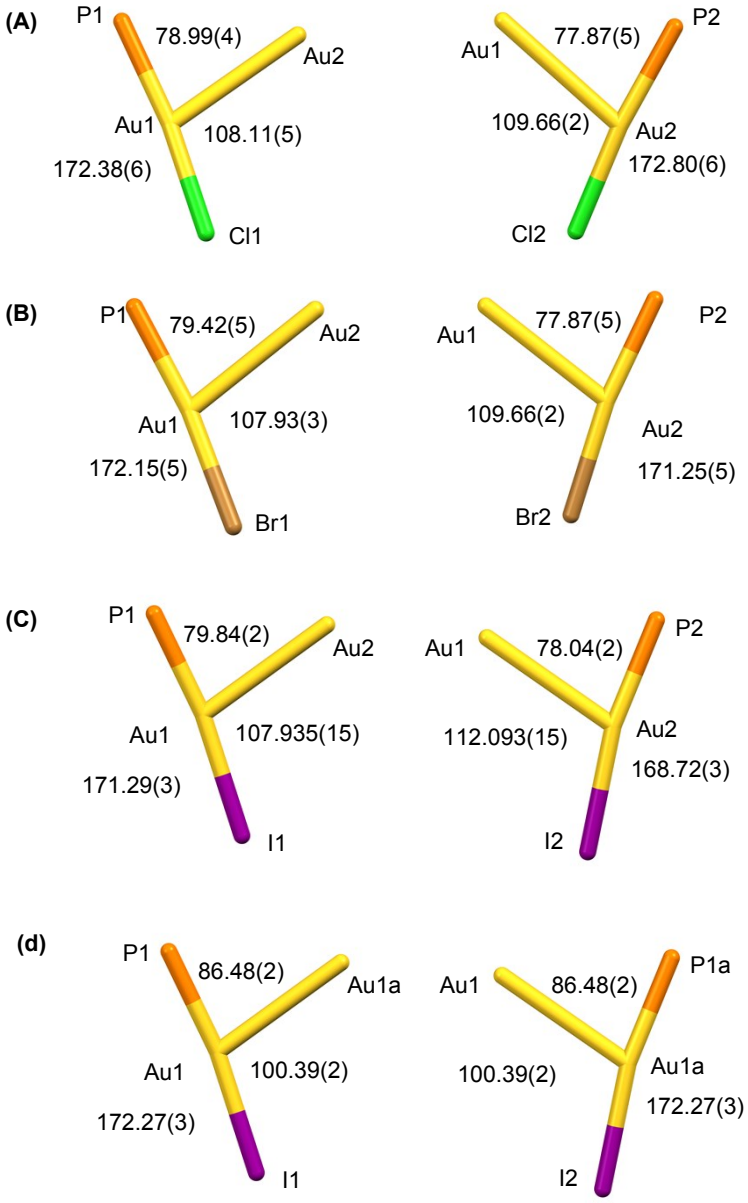


Fig. S2 Core structures of **1DOR**, **2DOR**, **3DOR** and **3DGR**.

4. NMR Experiments

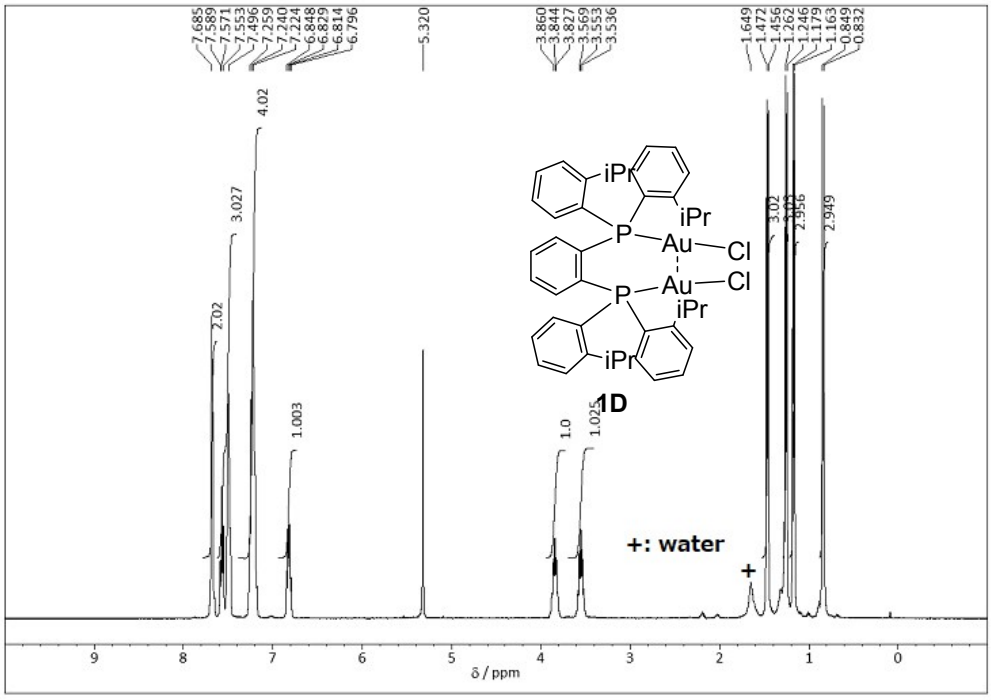


Fig. S3 ^{1}H NMR spectrum of **1D** in CD_2Cl_2 at 293 K.

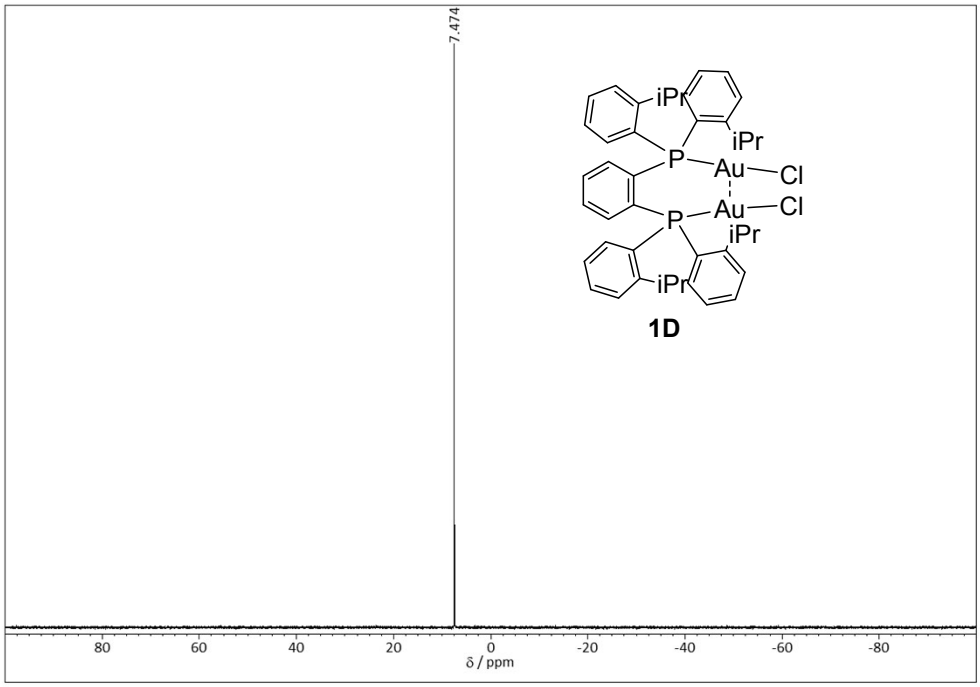


Fig. S4 ^{31}P $\{^{1}H\}$ NMR spectrum of **1D** in CD_2Cl_2 at 293 K.

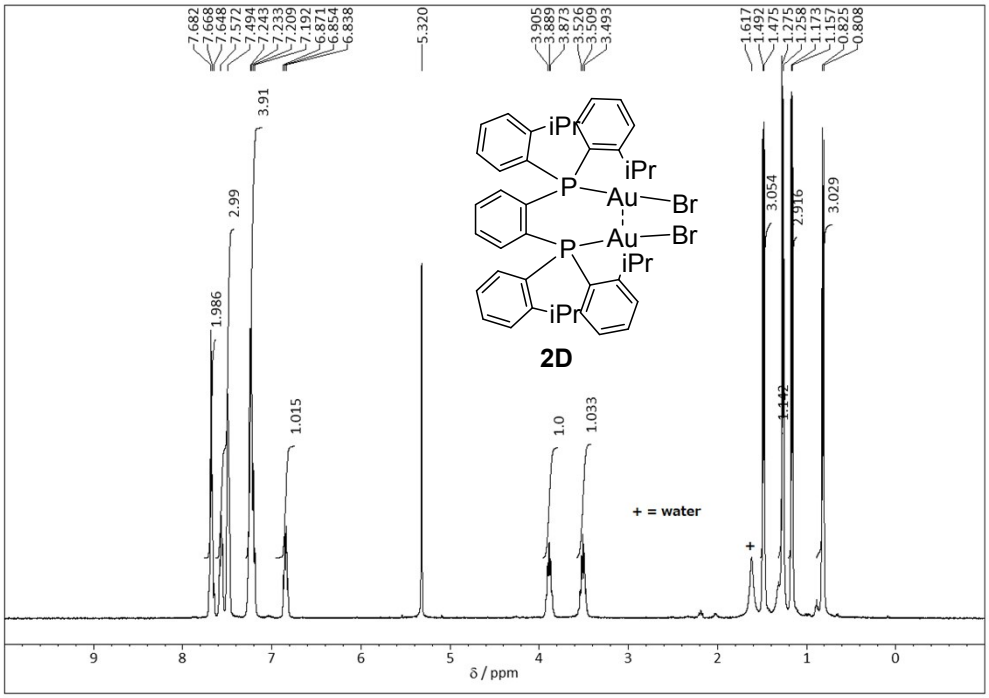


Fig. S5 ^{1}H NMR spectrum of **2D** in CD_2Cl_2 at 293 K.

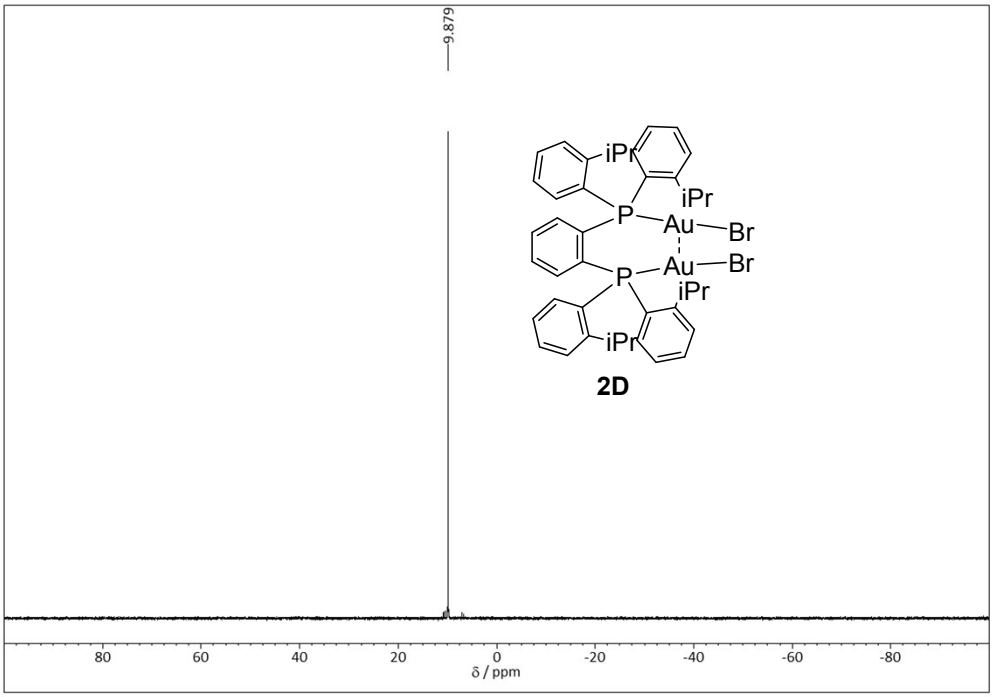


Fig. S6 ^{31}P $\{^{1}H\}$ NMR spectrum of **2D** in CD_2Cl_2 at 293 K.

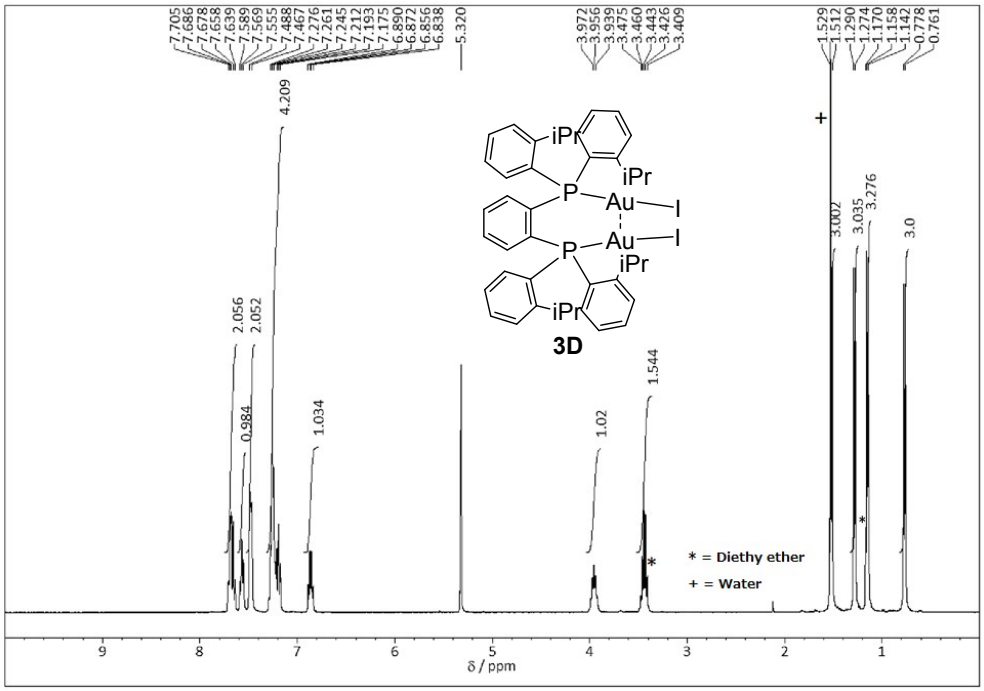


Fig. S7 ^{1}H NMR spectrum of **3D** in CD_2Cl_2 at 293 K.

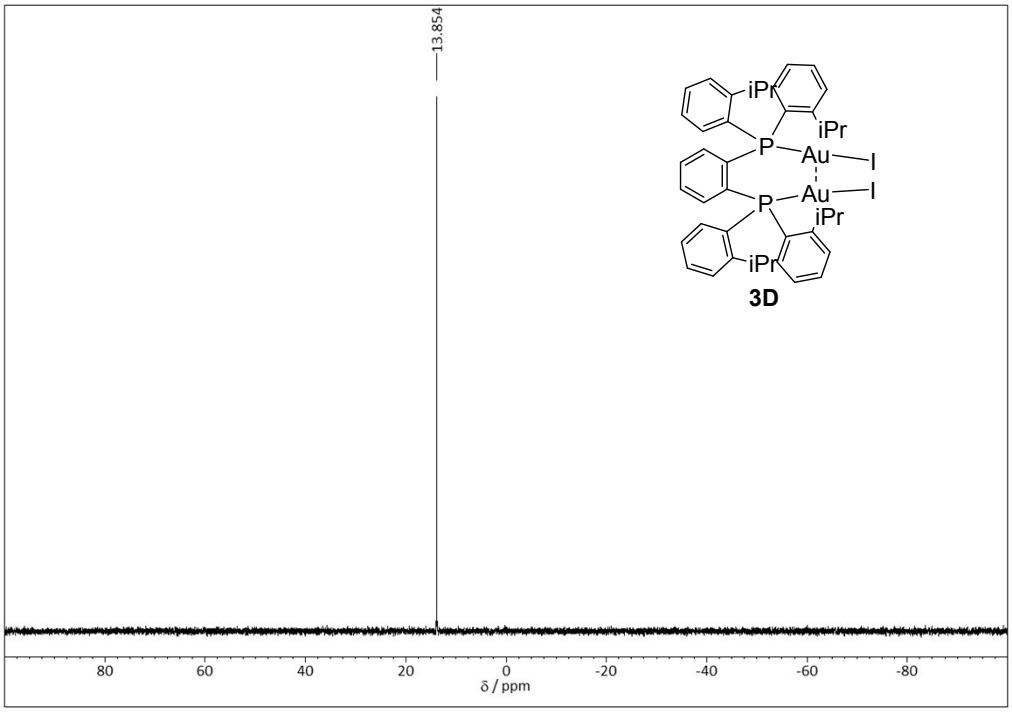


Fig. S8 ^{31}P $\{^{1}H\}$ NMR spectrum of **3D** in CD_2Cl_2 at 293 K.

7. Thermogravimetric Analyses

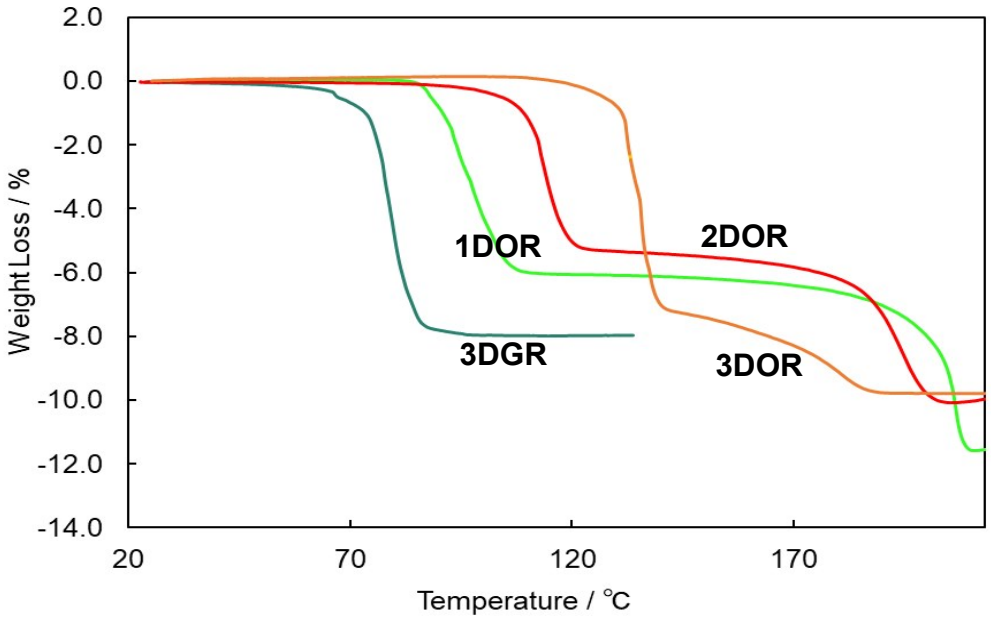


Fig. S9 TGA data for **1DOR** (green), **2DOR** (red), **3DOR** (orange), and **3DGR** (blue-green) under argon atmosphere with a heating rate of 20℃ min^{-1}.

4. Photophysical data

Table S3 Photophysical properties of **1** and **3** in crystals.

	293 K			77 K			
	λ_{max} / nm (eV) [a]	τ / μs[b]	Φ[c]	λ_{max} / nm (eV) [a]	τ / μs[b]	Φ[c]	$\Delta E_{S\text{-}T}$ / cm^{-1} (eV)
1	558(2.222)	13	0.82	582(2.130)	92	0.58	950(0.118)[d]
3	549(2.258)	9.0	0.92	569(2.179)	77	0.74	870(0.108)[d]

[a] Emission maxima; λ_{exc} =355 nm. [b] Emission decay time; λ_{exc} = 355nm. [c] Absolute PL quantum yield (error ± 8%); λ_{exc} = 355 nm. [d] Energy gap between S_1 and T_1 levels determined from the temperature dependence of the decay time.

Table S4 Rate constants and TADF-to-phosphorescence ratios for **1** and **3**.

							Φ(TADF) : Φ(Phos)	
	k_S (= $1/\tau_S$) / s^{-1}	k_T (= $1/\tau_T$) / s^{-1}	$k_S(r)$ / s^{-1}	$k_s(nr)$[a] / s^{-1}	$k_T(r)$ / s^{-1}	$k_T(nr)$[b] / s^{-1}	293 K	77 K
1	2.00 X 10^7	1.09 X 10^4	1.73 X 10^7	2.70 X 10^6	6.20 X 10^3	4.70 X 10^3	5 : 95	0 : 100
3	2.05 X 10^7	1.30 X 10^4	1.93 X 10^7	1.02 X 10^6	9.61 X 10^3	3.39 X 10^3	10 : 90	0 : 100

[a] $k_S(nr) = k_S - k_S(r)$, [b] $k_T(nr) = k_T - k_T(r)$

5. Theoretical Studies

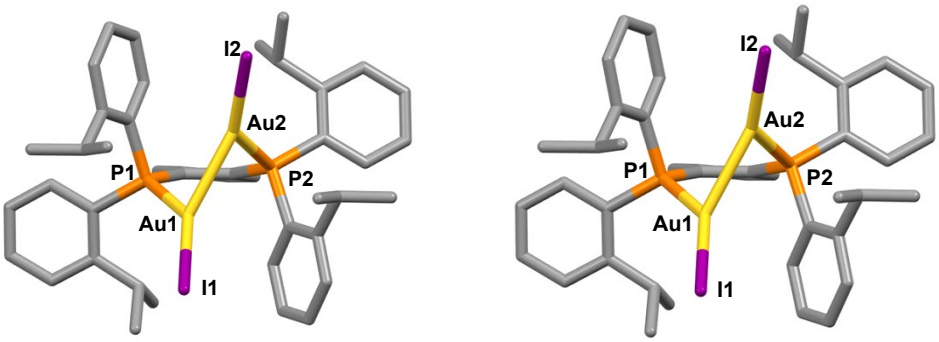


Fig. S10 DFT-optimized structures of **3DOR** (left) and **3DGR** (right) in T_1 states without crystallization solvents.

Table S5 Selected bond distances (Å) and angles (°) for **3DOR** and **3DGR** at T_1 optimized structures

	3DOR	**3DGR**
Au1–P1	2.476	2.477
Au1–I1	2.663	2.663
Au2–P2	2.477	2.477
Au2–I2	2.662	2.663
Au1–Au2	2.745	2.745
P1–Au1–I1	135.74	135.99
P1–Au1–Au2	80.77	80.85
Au2–Au1–I1	142.41	142.44
P2–Au2–I2	136.11	136.04
P2–Au2–Au1	80.83	80.85
Au1–Au2–I2	142.75	143.40

Table S6 Composition of hole and electron for **3DOR** at the T_1 optimized structure.[a]

	percentage composition (%) [b]		
	hole	electron	Difference
Au1	15	26	-11
Au2	14	26	-14
I1	21	8	13
I2	20	8	12
P1	11	8	3
P2	10	8	2
phenylene (L_{iPr})	3	8	-5

[a] The optimized T_1 geometry was obtained by unrestricted (U)-DFT. [b] The atomic component was evaluated by the Mulliken analysis.

Table S7 NTO analysis for selected transitions of **3DGR** at the T_1 optimized structures.

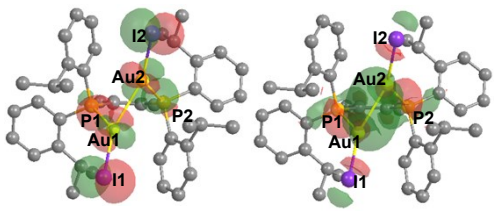
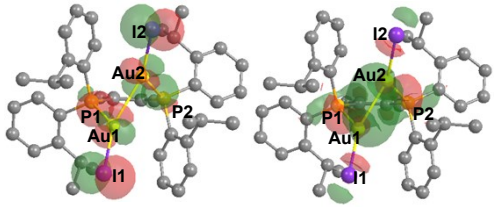
States	λ_{cal} / eV	*f*	NTO pairs Isovalue = 0.035		Generation probability (%)	Character
			Hole	Electron		
T_1	1.702	0.000			99	XMMCT MC
S_1	2.054	0.051			99	XMMCT MC

Table S8 Composition of hole and electron for **3DGR** at the T_1 optimized structure.[a]

	percentage composition (%) [b]		
	hole	electron	Difference
Au1	14	26	-12
Au2	14	26	-14
I1	21	8	13
I2	20	8	12
P1	10	8	2
P2	10	8	2
phenylene (L_{iPr})	3	9	-6

[a] The optimized T_1 geometry was obtained by unrestricted (U)-DFT. [b] The atomic component was evaluated by the Mulliken analysis.

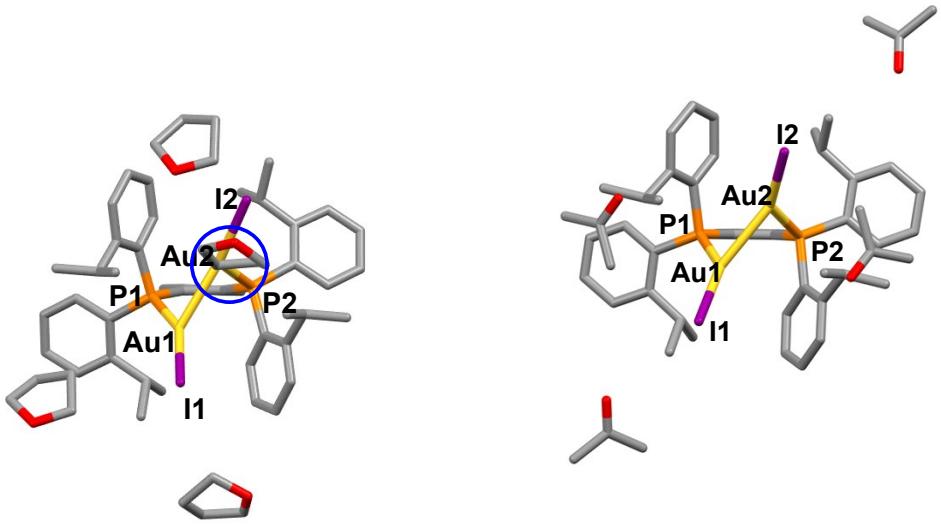


Fig. S11 DFT-optimized structures of **3DOR** (left) and **3DGR** (right) in T_1 states with crystallization solvents.

Table S9 Selected bond distances (Å) and angles (°) for **3DOR** and **3DGR** at T_1 optimized structures including crystalline solvent molecules.

	3DOR	**3DGR**
Au1–P1	2.434	2.490
Au1–I1	2.646	2.671
Au2–P2	2.503	2.491
Au2–I2	2.697	2.670
Au1–Au2	2.752	2.730
P1–Au1–I1	152.54	140.39
P1–Au1–Au2	80.80	81.02
Au2–Au1–I1	142.24	142.96
P2–Au2–I2	118.91	140.29
P2–Au2–Au1	84.65	80.83
Au1–Au2–I2	125.75	142.62

Table S10 NTO analysis for selected transitions of **3DOR** at the T_1 optimized structure with crystalline THF molecules.

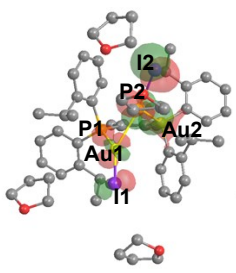
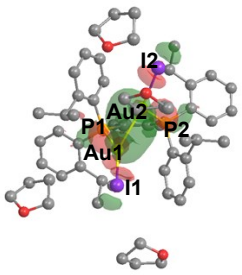
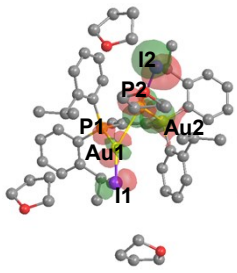
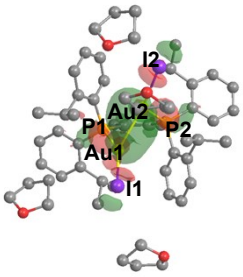
states	λ_{cal} / eV	*f*	NTO pairs Isovalue = 0.035		Generation probability (%)	Character
			Hole	Electron		
T_1	1.689	0.000			99	XMMCT MC
S_1	2.046	0.050			99	XXMCT MC

Table S11 Composition of hole and electron for **3DOR** at the T_1 optimized structure with crystalline THF molecules.

	percentage composition (%) [b]		
	hole	electron	Difference
Au1	9	22	-12
Au2	22	34	-12
I1	7	7	0
I2	30	9	21
P1	4	7	3
P2	17	8	9
phenylene (L_{iPr})	3	6	-3
THF	2	0	0

[a] The optimized T_1 geometry was obtained by unrestricted (U)-DFT. [b] The atomic component was evaluated by the Mulliken analysis.

Table S12 NTO analysis for selected transitions of **3DGR** at the T_1 optimized structure with crystalline acetone molecules.

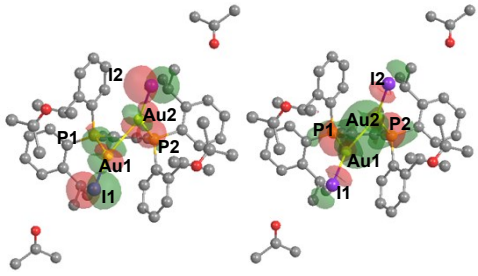
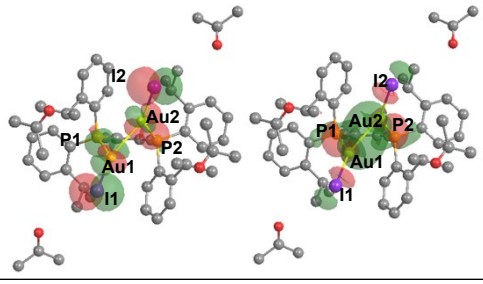
states	λ_{cal} / eV	*f*	NTO pairs Isovalue = 0.035		Generation probability (%)	Character
			Hole	Electron		
T_1	1.881	0.000			99	XMMCT MC
S_1	2.201	0.051			99	XMMCT MC

Table S13 Composition of hole and electron for **3DGR** at the T_1 optimized structure with crystalline acetone molecules.[a]

	percentage composition (%) [b]		
	hole	electron	Difference
Au1	14	25	-11
Au2	14	25	-11
I1	22	8	14
I2	22	8	14
P1	9	8	1
P2	9	8	2
phenylene (L_{iPr})	2	10	-8

[a] The optimized T_1 geometry was obtained by unrestricted (U)-DFT. [b] The atomic component was evaluated by the Mulliken analysis.

Table S14 Major single group excitation contributions for sublevels (M1, M2, and M3) in T_1 states for **3DOR**.

Excitation	Single group excited states		Excitation energy /eV	weight (sum=1)	Contribution to f
M1:	Triplet	1A	1.5993	0.9167	
M1:	Triplet	2A	2.2501	0.0194	
M1:	Triplet	2A	2.2501	0.0194	
M1:	Triplet	1A	1.5993	0.0128	
M1:	Triplet	1A	1.5993	0.0128	
M1:	Triplet	3A	2.3092	0.0035	
M1:	Triplet	3A	2.3092	0.0035	
M1:	Triplet	3A	2.3092	0.0025	
M1:	Triplet	4A	2.5527	0.0023	
M1:	Triplet	4A	2.5527	0.0023	
M1:	**Singlet**	**2A**	**2.3915**	**0.0013**	**0.3404E-05**
M1:	Triplet	2A	2.2501	0.0007	
M1:	Triplet	5A	2.5974	0.0005	
M1:	Triplet	5A	2.5974	0.0005	
M2:	Triplet	1A	1.5993	0.4713	
M2:	Triplet	1A	1.5993	0.4713	
M2:	Triplet	2A	2.2501	0.0404	
M2:	Triplet	3A	2.3092	0.0067	
M2:	**Singlet**	**4A**	**2.7289**	**0.0018**	**0.5470E-05**
M2:	Triplet	3A	2.3092	0.0012	
M2:	Triplet	3A	2.3092	0.0012	
M2:	Triplet	4A	2.5527	0.0010	
M2:	**Singlet**	**3A**	**2.6030**	**0.0010**	**0.6993E-05**
M2:	Triplet	1A	1.5993	0.0009	
M2:	Triplet	2A	2.2501	0.0004	
M2:	Triplet	2A	2.2501	0.0004	
M2:	Triplet	8A	3.1811	0.0003	

M2:	Triplet	8A	3.1811	0.0003	
M3:	Triplet	1A	1.5993	0.4675	
M3:	Triplet	1A	1.5993	0.4675	
M3:	**Singlet**	**2A**	**2.3915**	**0.0289**	**0.7500E-04**
M3:	Triplet	1A	1.5993	0.0248	
M3:	Triplet	4A	2.5527	0.0037	
M3:	Triplet	2A	2.2501	0.0008	
M3:	Triplet	2A	2.2501	0.0008	
M3:	**Singlet**	**3A**	**2.6030**	**0.0008**	**0.5758E-05**
M3:	Triplet	3A	2.3092	0.0008	
M3:	Triplet	3A	2.3092	0.0008	
M3:	Triplet	5A	2.5974	0.0007	
M3:	**Singlet**	**4A**	**2.7289**	**0.0003**	**0.1040E-05**
M3:	Triplet	8A	3.1811	0.0003	
M3:	Triplet	8A	3.1811	0.0003	

Table S15 Major single group excitation contributions for sublevels (M1, M2, and M3) in T_1 states for **3DGR**.

Excitation	Single group excited states		Excitation energy /eV	weight (sum=1)	Contribution to f
M1:	Triplet	1A	1.7571	0.4545	
M1:	Triplet	1A	1.7571	0.4545	
M1:	Triplet	2A	2.3788	0.0375	
M1:	Triplet	3A	2.4100	0.0238	
M1:	Triplet	2A	2.3788	0.0054	
M1:	Triplet	2A	2.3788	0.0054	
M1:	Triplet	1A	1.7571	0.0044	
M1:	Triplet	3A	2.4100	0.0042	
M1:	Triplet	3A	2.4100	0.0042	
M1:	Triplet	5A	2.6663	0.0015	
M1:	Triplet	5A	2.6663	0.0015	
M1:	**Singlet**	**2A**	**2.5186**	**0.0004**	**0.8591E-06**

M1:	Triplet	7A	3.0375	0.0004	
M1:	Triplet	8A	3.2132	0.0003	
M1:	Triplet	8A	3.2132	0.0003	
M2:	Triplet	1A	1.7571	0.8924	
M2:	Triplet	2A	2.3788	0.0225	
M2:	Triplet	2A	2.3788	0.0225	
M2:	Triplet	1A	1.7571	0.0138	
M2:	Triplet	1A	1.7571	0.0138	
M2:	**Singlet**	**3A**	**2.5734**	**0.0105**	**0.8128E-04**
M2:	Triplet	3A	2.4100	0.0099	
M2:	Triplet	3A	2.4100	0.0099	
M2:	Triplet	5A	2.6663	0.0013	
M2:	Triplet	2A	2.3788	0.0008	
M2:	Triplet	7A	3.0375	0.0004	
M2:	Triplet	7A	3.0375	0.0004	
M3:	Triplet	1A	1.7571	0.4545	
M3:	Triplet	1A	1.7571	0.4545	
M3:	**Singlet**	**2A**	**2.5186**	**0.0391**	**0.8369E-04**
M3:	Triplet	1A	1.7571	0.0237	
M3:	Triplet	3A	2.4100	0.0076	
M3:	Triplet	3A	2.4100	0.0076	
M3:	Triplet	2A	2.3788	0.0027	
M3:	Triplet	2A	2.3788	0.0027	
M3:	**Singlet**	**3A**	**2.5734**	**0.0019**	**0.1442E-04**
M3:	Triplet	5A	2.6663	0.0013	
M3:	Triplet	5A	2.6663	0.0013	
M3:	Triplet	7A	3.0375	0.0007	
M3:	Triplet	2A	2.3788	0.0004	
M3:	Triplet	8A	3.2132	0.0003	

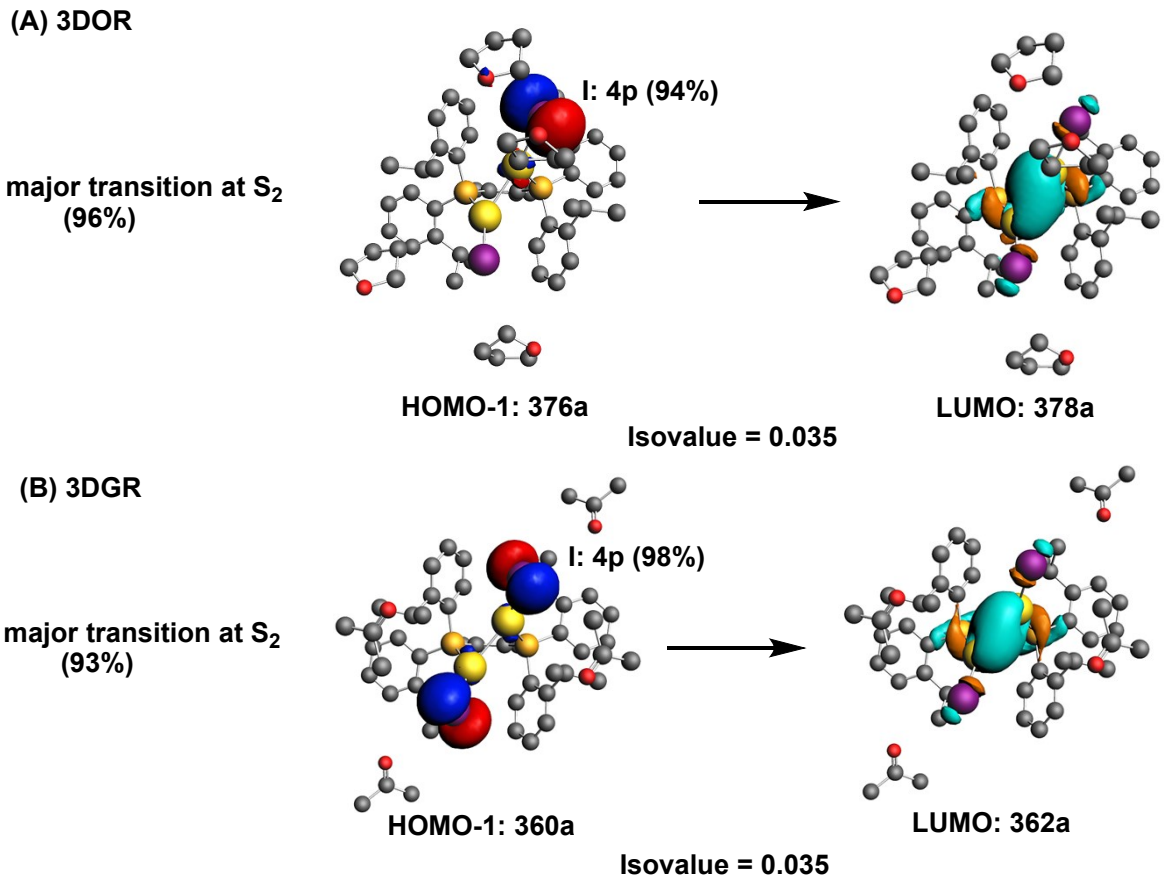


Fig. S12 Major transitions of S_2 states on T_1-optimized structures of (A) **3DOR** and (B) **3DGR**

Table S16 Geometry data of **3DOR** without crystalline solvents for the optimized T_1 state

Au	9.497733	5.992768	6.468470
Au	11.869571	4.661064	6.835550
I	12.993723	2.704742	8.248479
I	6.930318	5.622866	5.867964
P	12.465369	5.982386	4.828196
C	11.767617	7.190367	8.856830
C	11.070690	5.855157	3.639164
C	12.130099	8.493800	6.248251
C	11.167874	3.269373	3.663772
C	10.563208	4.596122	3.242527
C	13.168784	7.285556	8.873816
C	10.448521	7.033438	3.195403
C	9.118436	10.072277	7.149773
C	12.691099	7.780983	5.157143
C	11.092379	6.521561	9.904014
C	13.978370	5.549725	3.869502
C	9.322967	6.986104	2.380358
C	9.431596	4.581522	2.420074
C	9.155967	4.904937	9.921184
C	10.192217	2.438252	4.495887
C	10.013407	9.375226	7.992777
C	15.229498	5.438005	4.517281
C	12.523098	9.830649	6.447511
C	16.342301	5.110502	3.732687
C	13.883053	5.330045	2.486497
C	9.584108	6.370743	9.978583
C	8.806044	9.654185	5.724991
C	13.397717	10.478993	5.585897
C	11.868766	5.960882	10.923970
C	8.514420	11.229691	7.656398
P	10.851679	7.843363	7.404151
C	16.241599	4.889900	2.362844
C	15.434353	5.682669	6.000732
C	8.766226	11.691774	8.944228
C	13.257175	6.043120	10.927846
C	13.912793	6.715967	9.901229
C	11.668525	2.468661	2.463475
C	8.808333	5.751048	1.997558
C	16.125314	4.505826	6.681789
C	10.267139	9.848144	9.289716
C	9.007390	7.053010	11.217309
C	13.887660	9.801847	4.470428
C	9.438253	10.604420	4.709513
C	15.003978	4.999077	1.733093
C	9.648376	10.997530	9.768843
C	13.544735	8.470579	4.275470
C	16.193288	6.983413	6.256796
C	7.305797	9.521363	5.484631
H	12.050268	3.471495	4.306579
H	13.694394	7.804973	8.062465
H	10.842769	8.010920	3.500402
H	8.846696	7.916435	2.050245
H	9.014107	3.615745	2.109354
H	9.565303	4.391594	9.028742
H	8.052686	4.832544	9.873662
H	9.494974	4.348631	10.817148
H	9.811880	3.003087	5.369550
H	10.695698	1.529441	4.877080
H	9.319214	2.116671	3.894557
H	12.127397	10.385145	7.306543
H	17.325063	5.025785	4.213177
H	12.912458	5.435921	1.986016
H	9.134531	6.873089	9.096650
H	9.244192	8.648631	5.553990
H	13.684312	11.518307	5.781486
H	11.366451	5.427364	11.740483
H	7.821181	11.790583	7.017177
H	17.136343	4.633159	1.784021
H	14.437261	5.783833	6.477912
H	8.271450	12.601201	9.304294
H	13.829086	5.576625	11.737786
H	15.005929	6.794801	9.894178
H	10.835772	2.185857	1.790414
H	12.150138	1.532838	2.803862
H	12.410057	3.032681	1.867269
H	7.914067	5.695357	1.366758
H	15.600450	3.553433	6.478560
H	16.133705	4.647930	7.779259
H	17.177351	4.399960	6.351365
H	10.976997	9.313431	9.933058
H	9.373097	6.577786	12.148346
H	7.904131	6.973009	11.217370
H	9.268133	8.127256	11.259463
H	14.549290	10.303833	3.755694
H	9.038743	11.632075	4.820639
H	9.210863	10.272289	3.677695
H	10.538748	10.658132	4.816481
H	14.909612	4.834842	0.653535
H	9.862540	11.352867	10.783328
H	13.959148	7.945253	3.406978
H	17.208349	6.949013	5.813471
H	16.314043	7.150765	7.344967
H	15.670350	7.861942	5.832421
H	6.831091	8.859691	6.233356
H	7.114602	9.079037	4.488385
H	6.795515	10.504113	5.516227

Table S17 Geometry data of **3DGR** without crystalline solvents for the optimized T_1 state

Au	21.731935	22.692097	15.669754
I	21.820362	24.932293	14.232955
P	20.430968	21.870739	17.611539
C	19.053463	22.895617	18.280659
C	20.617874	24.937000	18.530392
C	19.271648	24.245186	18.638314
C	20.530047	26.227401	17.722036

C 17.779580 22.326790 18.434818
C 21.448366 21.527415 19.108420
C 19.118552 21.141907 13.654530
C 19.670606 20.266056 17.139917
C 18.897576 20.143263 15.962057
C 18.541451 21.309995 15.059324
C 21.453367 21.487566 21.554849
C 16.716386 23.070815 18.934416
C 18.184827 24.968415 19.145601
C 19.940900 19.132233 17.923390
C 16.923150 24.400752 19.292580
C 20.783796 21.620473 20.345756
C 21.230567 25.194111 19.905828
C 18.442669 18.866838 15.613824
C 19.473276 17.876741 17.551274
C 17.032441 21.537543 14.997688
C 18.727800 17.743986 16.383659
P 23.855754 20.895953 17.612447
C 25.232995 19.871436 18.282654
C 23.668440 17.830215 18.532847
C 25.014635 18.522064 18.640947
C 23.756512 16.539688 17.724720
C 26.506839 20.440302 18.436969
C 22.837765 21.240024 19.108773
C 25.169504 21.622790 13.655416
C 24.616280 22.500407 17.140276
C 25.389575 22.622652 15.962528
C 25.746046 21.455462 15.060529
C 22.831690 21.280855 21.555188
C 27.569831 19.696499 18.937331
C 26.101246 17.799063 19.149004
C 24.345785 23.634604 17.923134
C 27.362893 18.366759 19.296126
C 23.501792 21.147474 20.346439
C 23.055384 17.573372 19.908166
C 25.844449 23.898936 15.613729
C 24.813417 24.889940 17.550489
C 27.255084 21.227896 14.999605
C 25.559083 25.022160 16.382936
Au 22.555699 20.073116 15.670763
I 22.466306 17.832727 14.234457
H 21.311180 24.265734 17.981635
H 19.948649 27.006511 18.253198
H 21.541898 26.635266 17.536930
H 20.060511 26.056600 16.735014
H 17.620231 21.273525 18.172278
H 18.647964 20.292024 13.122201
H 18.939126 22.056625 13.058040
H 20.211706 20.964530 13.677178
H 18.988941 22.233223 15.483564
H 20.896848 21.558961 22.496009
H 15.729860 22.607519 19.050294
H 18.332531 26.015930 19.436801
H 20.537930 19.226651 18.839225
H 16.097530 25.001494 19.691328
H 19.703544 21.806893 20.363473
H 21.375537 24.258386 20.479410
H 22.216714 25.687249 19.801983
H 20.589074 25.864646 20.511481
H 17.852373 18.745800 14.697041
H 19.697483 17.002357 18.172832
H 16.511454 20.672783 14.542401
H 16.596351 21.707579 15.999974
H 16.806066 22.424108 14.376074
H 18.364403 16.759611 16.067933
H 22.975241 18.501356 17.983806
H 24.337935 15.760736 18.256085
H 22.744734 16.131679 17.539530
H 24.226164 16.710389 16.737733
H 26.666314 21.493424 18.173933
H 25.640409 22.472289 13.122755
H 25.349036 20.707693 13.059540
H 24.076363 21.800306 13.677543
H 25.298395 20.532456 15.485086
H 23.387801 21.209833 22.496618
H 28.556334 20.159819 19.053312
H 25.953400 16.751707 19.440707
H 23.748585 23.540607 18.838899
H 28.188352 17.766200 19.695483
H 24.582039 20.961066 20.364702
H 22.910369 18.509212 20.481552
H 22.069201 17.080341 19.804140
H 23.696632 16.902857 20.514099
H 26.434918 24.019552 14.697002
H 24.589064 25.764617 18.171582
H 27.776242 22.092445 14.544110
H 27.690774 21.058348 16.002144
H 27.481714 20.341034 14.378508
H 25.922470 26.006401 16.066779

Table S18 Geometry data of **3DOR** with crystalline THF molecules for the optimized T_1 state

Au 9.303023 5.825985 6.627215
Au 11.575580 4.286694 6.820982
I 12.984469 2.113367 7.572685
I 6.879606 4.937853 6.044317
P 12.363287 5.618533 4.853952
C 11.749210 6.815558 8.934641
C 10.959117 5.592458 3.673957
C 12.144277 8.112477 6.334867
C 10.975301 3.012476 3.555491
C 10.394924 4.375003 3.228850
C 13.153062 6.791194 8.891882
C 10.366154 6.813415 3.308186
C 9.234830 9.809642 7.155428
C 12.658096 7.400983 5.223566
C 11.068180 6.169449 9.992426
C 13.875663 5.146854 3.920320

C	9.217581	6.844495	2.526166
C	9.234506	4.441599	2.449164
C	9.015527	4.707729	10.057843
C	10.022493	2.167696	4.398796
C	10.060665	9.082115	8.043266
C	15.120103	5.003838	4.577328
C	12.599051	9.425632	6.554684
C	16.230493	4.668425	3.792694
C	13.783583	4.945320	2.534577
C	9.558066	6.134554	10.134838
C	8.976732	9.391171	5.718808
C	13.478403	10.058230	5.685435
C	11.838559	5.505897	10.954539
C	8.665489	10.999583	7.623037
P	10.837697	7.505592	7.493254
C	16.133932	4.467753	2.419292
C	15.320374	5.225262	6.065996
C	8.890873	11.468096	8.914485
C	13.227189	5.461471	10.890802
C	13.891240	6.116940	9.858436
C	11.384790	2.254707	2.294033
C	8.637037	5.650075	2.104033
C	16.118500	4.099764	6.718739
C	10.285869	9.558528	9.342273
C	9.095058	6.821439	11.418422
C	13.908532	9.389641	4.541476
C	9.605209	10.364049	4.723431
C	14.902523	4.604454	1.783210
C	9.705241	10.744368	9.781854
C	13.513099	8.075141	4.331602
C	15.987995	6.569299	6.358307
C	7.493445	9.192961	5.425598
H	11.896928	3.156876	4.157069
H	13.688005	7.292403	8.075513
H	10.804636	7.761583	3.643035
H	8.769070	7.810142	2.256561
H	8.769140	3.507809	2.110214
H	9.359174	4.188983	9.141196
H	7.908682	4.717779	10.040110
H	9.333890	4.102292	10.928975
H	9.707885	2.694082	5.321998
H	10.523802	1.228379	4.699780
H	9.105937	1.903842	3.835251
H	12.245782	9.976835	7.434125
H	17.208674	4.557369	4.276349
H	12.817286	5.076227	2.031711
H	9.110392	6.698010	9.289526
H	9.457581	8.405978	5.551786
H	13.811811	11.080447	5.896350
H	11.328139	4.990522	11.777689
H	8.025073	11.583787	6.949419
H	17.027862	4.202768	1.843037
H	14.321498	5.234229	6.551542
H	8.428380	12.406002	9.243144
H	13.792014	4.914173	11.654323
H	14.985891	6.100311	9.797070
H	10.506837	2.018514	1.662162
H	11.863990	1.295433	2.565454
H	12.101331	2.827384	1.676084
H	7.703954	5.660106	1.523764
H	15.719868	3.103483	6.453385
H	16.070476	4.191594	7.820641
H	17.187690	4.136490	6.431249
H	10.946420	8.998555	10.016583
H	9.474634	6.298842	12.317887
H	7.989721	6.814594	11.479396
H	9.430022	7.874777	11.471984
H	14.568743	9.881473	3.818547
H	9.147431	11.370553	4.792595
H	9.451766	10.002825	3.687031
H	10.694233	10.475953	4.886853
H	14.811338	4.453958	0.701486
H	9.897971	11.105189	10.798772
H	13.888456	7.550943	3.444877
H	16.995953	6.617910	5.900259
H	16.115716	6.702140	7.450995
H	15.404647	7.427583	5.976726
H	7.041496	8.436013	6.093971
H	7.363699	8.828619	4.387366
H	6.920060	10.136098	5.525201
O	8.558996	-2.070995	8.721992
C	8.635081	-1.907963	7.294069
C	9.399025	-0.622980	7.099082
C	8.822008	0.253877	8.215994
C	8.388027	-0.759022	9.276894
H	7.728961	-1.843009	6.898968
H	9.112002	-2.669053	6.877972
H	9.227854	-0.231912	6.206935
H	10.373060	-0.761002	7.214005
H	9.508029	0.871023	8.574018
H	8.050975	0.782038	7.890976
H	8.939008	-0.656987	10.093046
H	7.437955	-0.611983	9.520026
O	4.098007	8.250999	9.305013
C	6.383927	7.774980	8.934929
C	4.866036	9.058951	10.191910
C	6.237927	9.141910	9.585995
C	4.976050	7.534036	8.434067
H	7.035061	7.797004	8.189970
H	6.659972	7.088035	9.592081
H	4.905998	8.647996	11.091052
H	4.466979	9.962042	10.272019
H	6.929044	9.286022	10.281032
H	6.293012	9.868040	8.916982
H	4.879983	7.858028	7.504970
H	4.764992	6.565958	8.454985
O	5.509096	6.440049	1.472172
C	5.432912	6.603025	2.899900

C	4.669027	7.887730	3.094035
C	5.246065	8.763840	1.977807
C	5.680905	7.751903	0.916972
H	6.339021	6.667986	3.295034
H	4.956962	5.841940	3.315962
H	4.841176	8.279413	3.986815
H	3.694949	7.749932	2.980086
H	4.560060	9.382084	1.619947
H	6.017790	9.292047	2.303334
H	5.128995	7.853006	0.100958
H	6.630042	7.898053	0.673001
O	11.131999	0.259987	11.083007
C	13.418994	0.734993	11.452999
C	11.901002	-0.547997	10.196007
C	13.271996	-0.631995	10.801002
C	12.010005	0.976993	11.952992
H	14.070005	0.714001	12.198010
H	13.694003	1.423006	10.795990
H	11.940003	-0.137992	9.296989
H	11.500994	-1.451008	10.116001
H	13.963007	-0.775000	10.106992
H	13.327997	-1.357006	11.471010
H	11.913995	0.653000	12.883009
H	11.799002	1.945014	11.932990

Table S19 Geometry data of **3DGR** with crystalline acetone molecules for the optimized T_1 state

Au	9.340000	5.817000	6.509000
Au	11.602000	4.299000	6.890000
I	13.062000	2.187000	7.715000
I	6.917000	5.187000	5.650000
P	12.496000	5.586000	4.949000
C	11.731000	6.812000	8.940000
C	11.181000	5.428000	3.681000
C	12.138000	8.120000	6.344000
C	11.380000	2.849000	3.665000
C	10.759000	4.159000	3.220000
C	13.134000	6.858000	8.950000
C	10.519000	6.589000	3.246000
C	9.199000	9.805000	7.201000
C	12.690000	7.395000	5.259000
C	11.043000	6.125000	9.968000
C	14.084000	5.146000	4.126000
C	9.447000	6.513000	2.365000
C	9.690000	4.118000	2.319000
C	9.008000	4.625000	9.975000
C	10.374000	1.997000	4.438000
C	10.044000	9.067000	8.063000
C	15.291000	5.078000	4.859000
C	12.549000	9.452000	6.532000
C	16.457000	4.743000	4.160000
C	14.086000	4.885000	2.747000
C	9.532000	6.057000	10.072000
C	8.881000	9.396000	5.773000
C	13.419000	10.088000	5.656000
C	11.808000	5.480000	10.946000
C	8.659000	11.001000	7.688000
P	10.828000	7.500000	7.492000
C	16.451000	4.479000	2.794000
C	15.397000	5.388000	6.341000
C	8.924000	11.466000	8.972000
C	13.198000	5.502000	10.934000
C	13.867000	6.207000	9.938000
C	11.968000	2.050000	2.506000
C	9.030000	5.268000	1.900000
C	16.178000	4.324000	7.108000
C	10.304000	9.538000	9.359000
C	9.035000	6.729000	11.352000
C	13.883000	9.404000	4.535000
C	9.547000	10.324000	4.758000
C	15.258000	4.551000	2.080000
C	9.749000	10.728000	9.817000
C	13.532000	8.072000	4.357000
C	16.022000	6.763000	6.576000
C	7.380000	9.303000	5.518000
H	12.215000	3.073000	4.360000
H	13.672000	7.402000	8.164000
H	10.837000	7.575000	3.609000
H	8.935000	7.427000	2.044000
H	9.350000	3.142000	1.950000
H	9.372000	4.116000	9.061000
H	7.901000	4.625000	9.938000
H	9.316000	4.015000	10.847000
H	9.958000	2.536000	5.313000
H	10.864000	1.075000	4.806000
H	9.524000	1.699000	3.793000
H	12.166000	10.018000	7.390000
H	17.406000	4.687000	4.707000
H	13.150000	4.959000	2.180000
H	9.095000	6.620000	9.221000
H	9.290000	8.378000	5.605000
H	13.717000	11.126000	5.842000
H	11.292000	4.930000	11.744000
H	8.007000	11.594000	7.033000
H	17.386000	4.216000	2.286000
H	14.372000	5.405000	6.767000
H	8.482000	12.411000	9.313000
H	13.760000	4.970000	11.710000
H	14.963000	6.249000	9.923000
H	11.181000	1.610000	1.862000
H	12.555000	1.199000	2.901000
H	12.643000	2.657000	1.874000
H	8.181000	5.191000	1.211000
H	15.829000	3.304000	6.866000
H	16.043000	4.468000	8.197000
H	17.264000	4.383000	6.898000
H	10.975000	8.971000	10.016000
H	9.413000	6.210000	12.254000

H	7.930000	6.698000	11.396000
H	9.348000	7.789000	11.414000
H	14.535000	9.898000	3.806000
H	9.176000	11.363000	4.860000
H	9.319000	9.993000	3.726000
H	10.647000	10.345000	4.873000
H	15.237000	4.351000	1.002000
H	9.971000	11.083000	10.830000
H	13.936000	7.535000	3.491000
H	17.047000	6.806000	6.158000
H	16.101000	6.972000	7.661000
H	15.438000	7.580000	6.112000
H	6.881000	8.634000	6.244000
H	7.189000	8.882000	4.512000
H	6.890000	10.295000	5.565000
O	8.559000	-2.071000	8.722000
C	8.635000	-1.908000	7.294000
C	9.399000	-0.623000	7.099000
C	8.822000	0.254000	8.216000
C	8.388000	-0.759000	9.277000
H	7.729000	-1.843000	6.899000
H	9.112000	-2.669000	6.878000
H	9.228000	-0.232000	6.207000
H	10.373000	-0.761000	7.214000
H	9.508000	0.871000	8.574000
H	8.051000	0.782000	7.891000
H	8.939000	-0.657000	10.093000
H	7.438000	-0.612000	9.520000
O	4.098000	8.251000	9.305000
C	6.384000	7.775000	8.935000
C	4.866000	9.059000	10.192000
C	6.238000	9.142000	9.586000
C	4.976000	7.534000	8.434000
H	7.035000	7.797000	8.190000
H	6.660000	7.088000	9.592000
H	4.906000	8.648000	11.091000
H	4.467000	9.962000	10.272000
H	6.929000	9.286000	10.281000
H	6.293000	9.868000	8.917000
H	4.880000	7.858000	7.505000
H	4.765000	6.566000	8.455000
O	9.971000	-0.260000	0.889000
C	7.685000	-0.736000	1.259000
C	9.203000	0.548000	0.002000
C	7.831000	0.631000	0.608000
C	9.093000	-0.977000	1.760000
H	7.034000	-0.714000	2.004000
H	7.409000	-1.423000	0.602000
H	9.163000	0.137000	-0.897000
H	9.602000	1.451000	-0.078000
H	7.140000	0.775000	-0.087000
H	7.776000	1.357000	1.277000
H	9.189000	-0.653000	2.689000
H	9.304000	-1.945000	1.739000
O	11.132000	0.260000	11.083000
C	13.419000	0.735000	11.453000
C	11.901000	-0.548000	10.196000
C	13.272000	-0.632000	10.801000
C	12.010000	0.977000	11.953000
H	14.070000	0.714000	12.198000
H	13.694000	1.423000	10.796000
H	11.940000	-0.138000	9.297000
H	11.501000	-1.451000	10.116000
H	13.963000	-0.775000	10.107000
H	13.328000	-1.357000	11.471000
H	11.914000	0.653000	12.883000
H	11.799000	1.945000	11.933000

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