Electronic Supplementary Information for:

Photophysical Properties of Palladium/Platinum Tetrasulfonyl Phthalocyanines and Their Application in Triplet-Triplet-Annihilation Upconversion

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1. Changes in UV/Vis Absorption Spectra at Different Concentrations

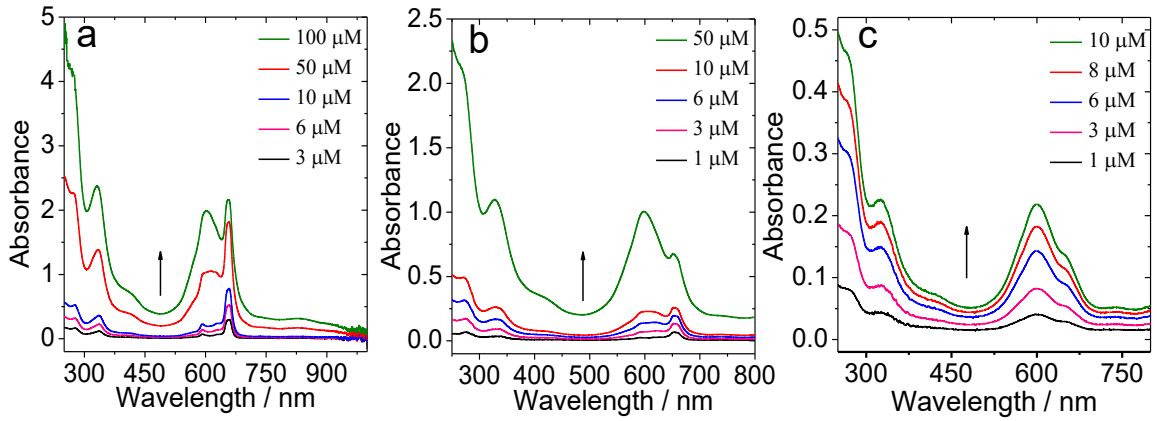

Fig. S1 UV–vis absorption of **Pd-Pc** (a) in chloroform, (b) in THF and (c) in acetonitrile at 20 °C.

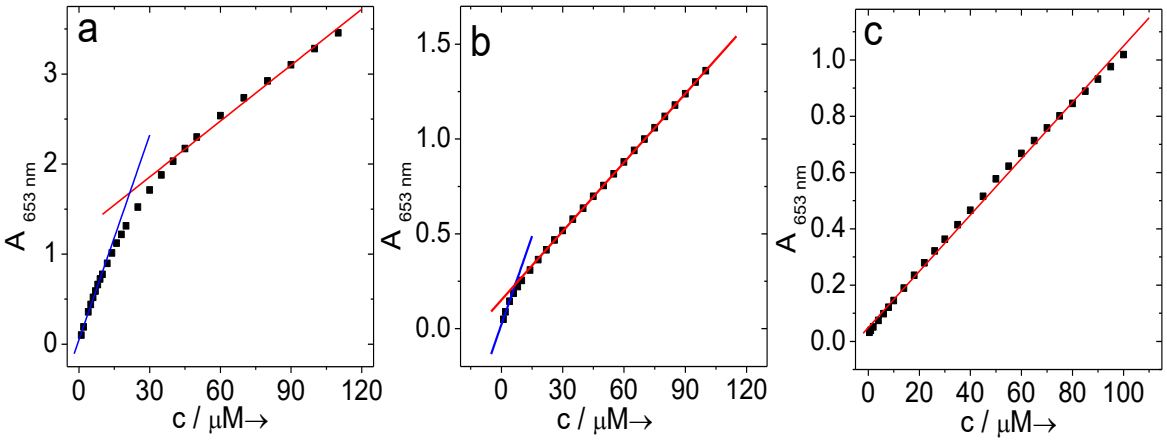

Fig. S2 Absorbance vs concentration of **Pd-Pc** (a) in chloroform, (b) in THF and (c) in acetonitrile at 653 nm at 20°C.

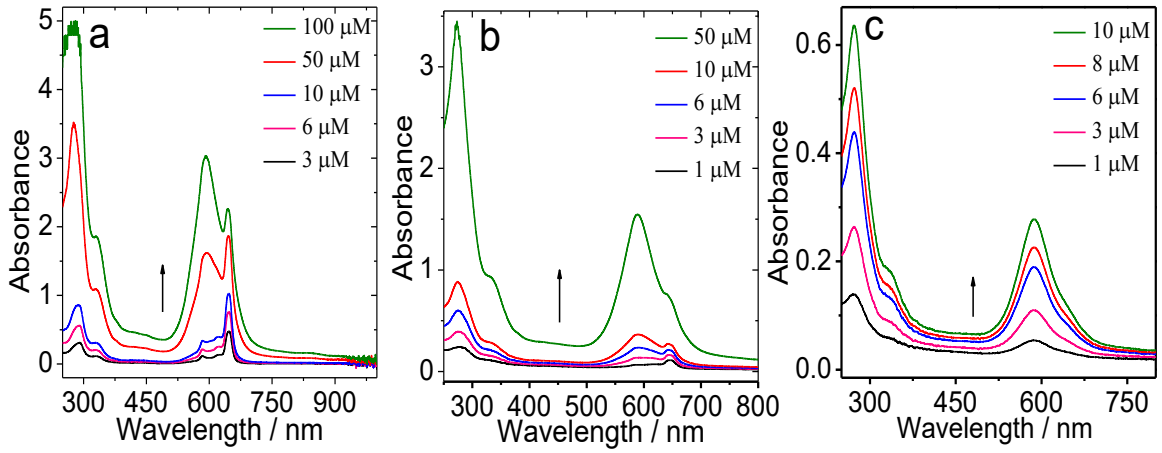

Fig. S3 UV–vis absorption of **Pt-Pc** (a) in chloroform, (b) in THF and (c) in acetonitrile at 20 °C.

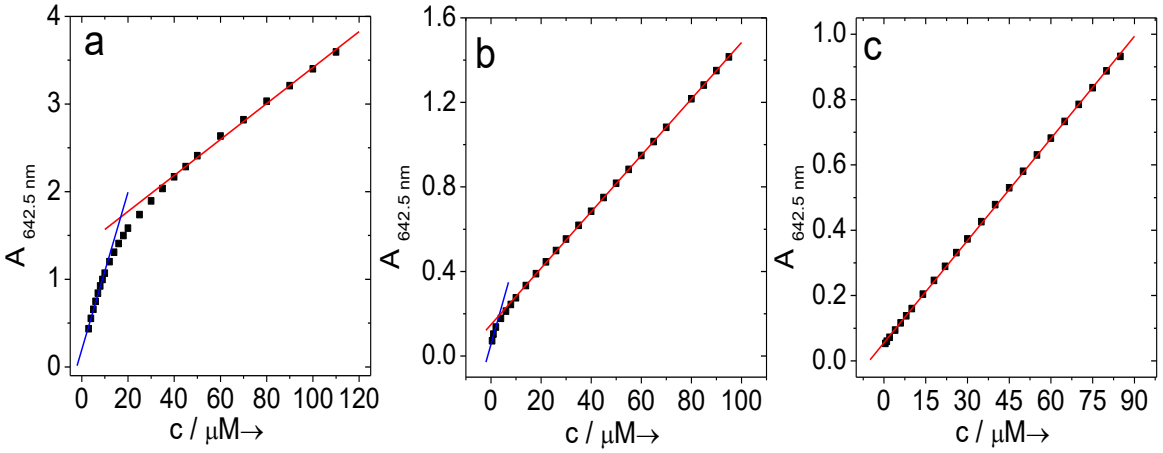

Fig. S4 Absorbance vs concentration of **Pt-Pc** (a) in chloroform, (b) in THF and (c) in acetonitrile at 653 nm, at 20 °C.

2. Nanosecond Transient Absorption Spectroscopy in THF

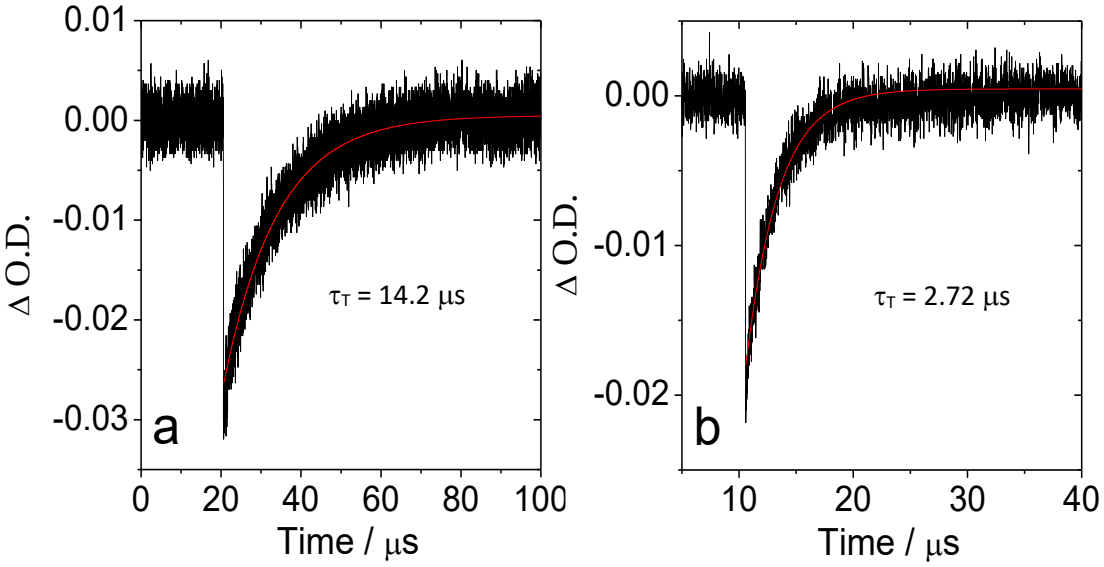

Fig. S5 (a) Decay trace of **Pd-Pc** at 658 nm. (b) Decay trace of **Pt-Pc** at 647 nm. $c = 1.0 \times 10^{-5}$ M in deaerated THF at20 °C.

3. TTA Upconversion of Photosensitizers Upon the Addition of Acceptor

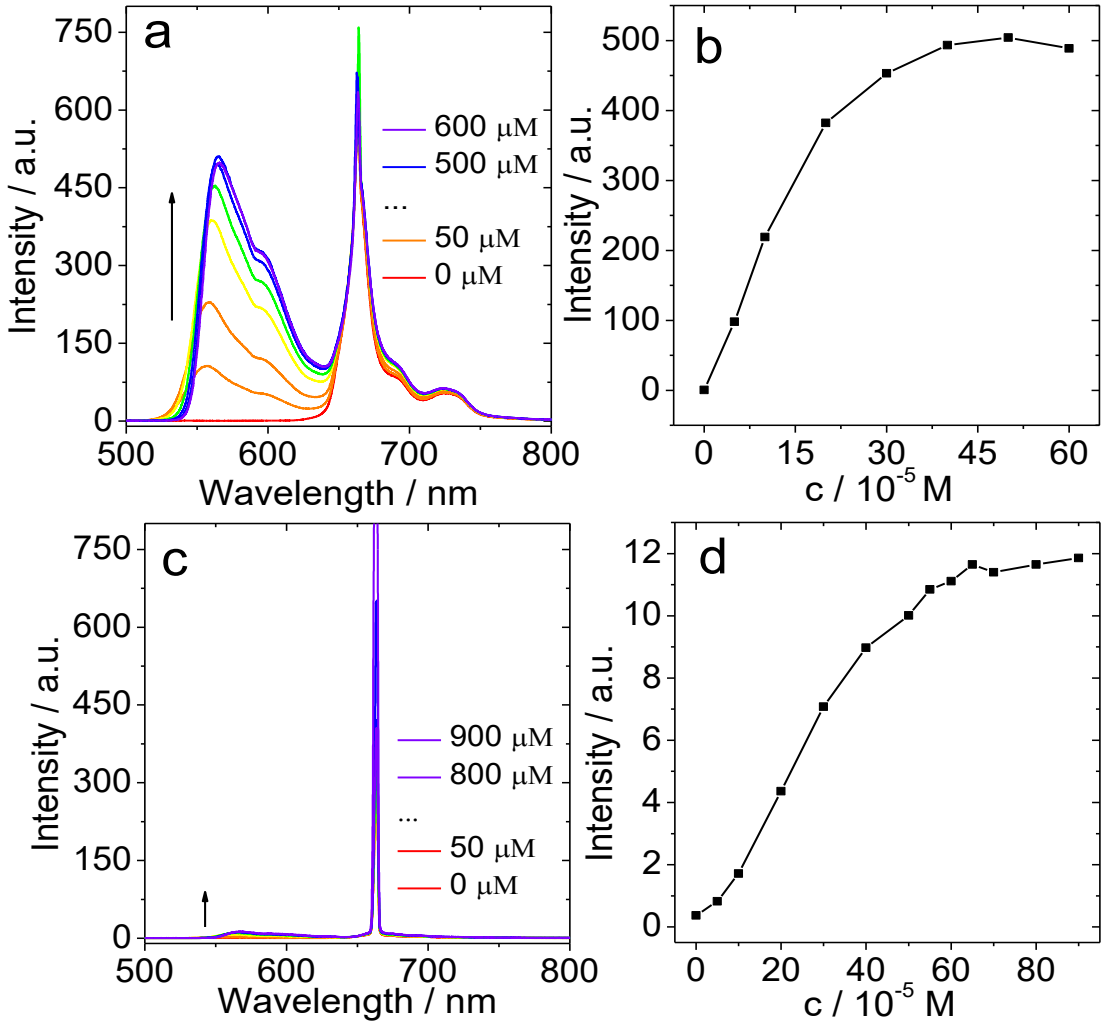

Fig. S6 The TTA upconversion fluorescence spectral of **Pd-Pc** (a) and **Pt-Pc** (c) as the triplet photosensitizers and R as the triplet acceptor. The upconversion intensity of **Pd-Pc** (b) and **Pt-Pc** (d) upon the addition of **R**. Excited with 658 nm cw-laser (1115 mW cm^{-2}). *c*[sensitizers] = 1.0 × 10^{-5} M in deaerated chloroform at 20 °C.

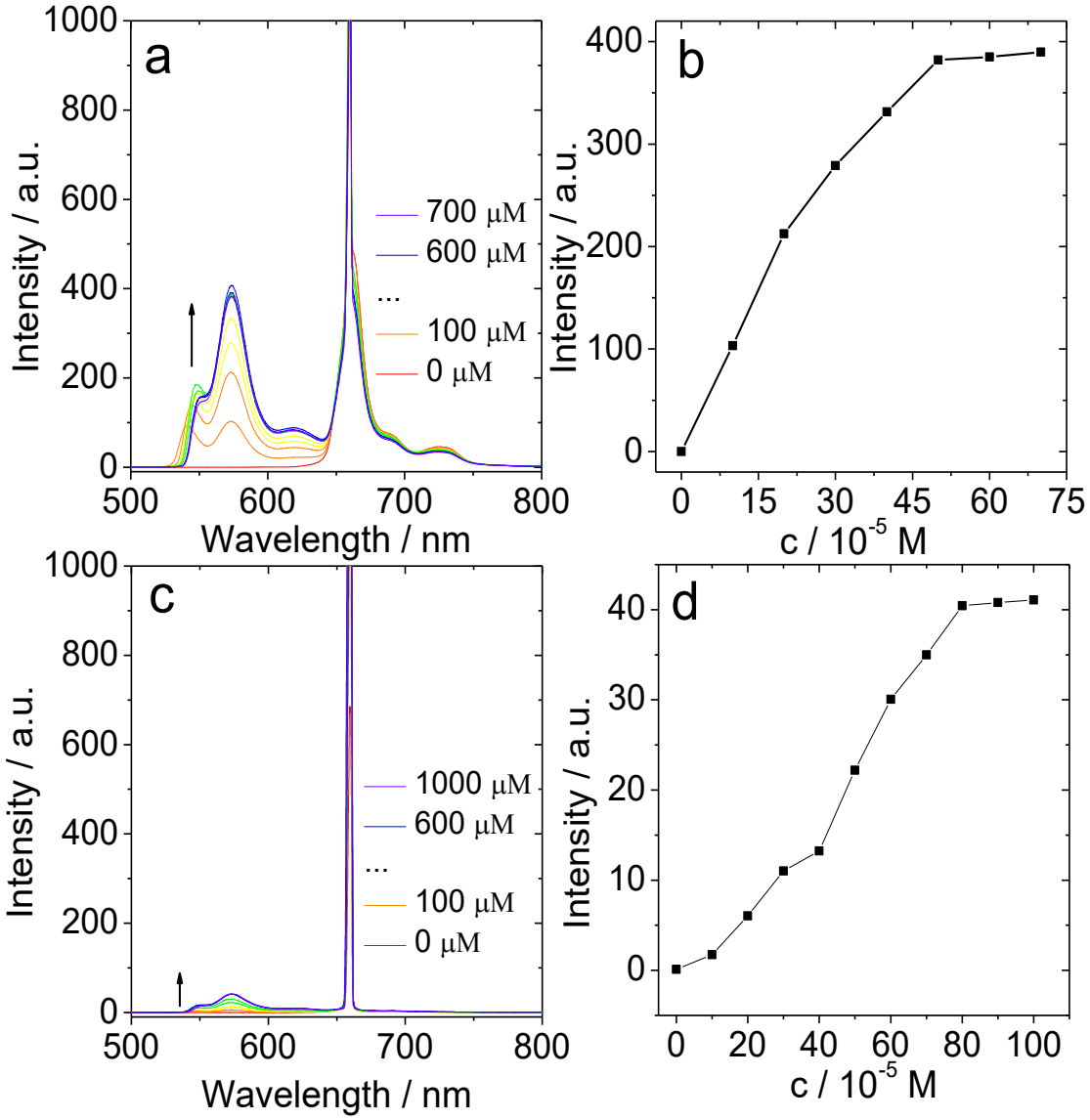

Fig. S7 The TTA upconversion fluorescence spectral of **Pd-Pc** (a) and **Pt-Pc** (c) as the triplet photosensitizers and PBI as the triplet acceptor, the upconversion intensity of **Pd-Pc** (b) and **Pt-Pc** (d) upon the addition of **PBI**. Excited with 658 nm cw-laser (1115 mW cm^{-2}). *c*[sensitizers] = 1.0×10^{-5} M in deaerated chloroform at 20 °C.

4. Changes of TTA upconversion fluorescence spectral with different laser power

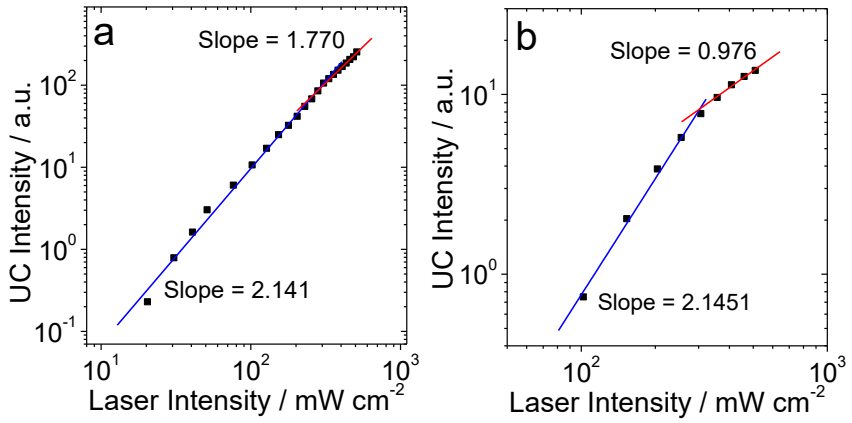

Fig. S8 Integrated emission intensity plotted as a function of normalized incident light power of **Pd-Pc** (a) and **Pt-Pc** (b) as the triplet photosensitizers and **R** as the triplet acceptor. Excited with a 658 nm cw-laser. *c*[sensitizers] = 1.0×10^{-5} M in deaerated chloroform at 20 °C.

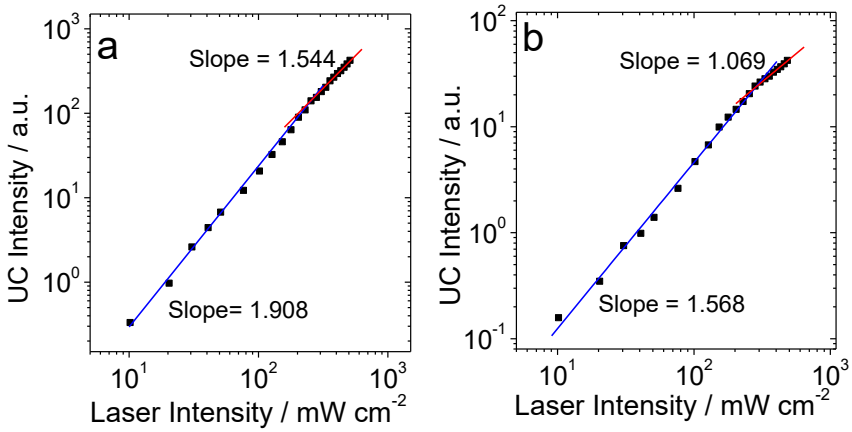

Fig. S9. Integrated emission intensity plotted as a function of normalized incident light power of **Pd-Pc** (a) and **Pt-Pc** (b) as the triplet photosensitizers and **PBI** as the triplet acceptor. Excited with a 658 nm cw-laser. *c*[sensitizers] = 1.0×10^{-5} M in deaerated chloroform at 20 °C.

5. The Intermolecular Triplet State Energy Transfer

Table S1. Kinetics of the Intermolecular Triplet State Energy Transfer between **Pt-Pc** and **1CBPEA**.

molar ratio Pt-Pc : R	$\tau_{1\ 647}$ nm [a] (μs)	$\tau_{2\ 647}$ nm [b] (μs)	k_{ET} [c] (μs^{-1})	Φ_{ET} % [d]
1:0	–	2.99	–	–
1:9	0.136	2.85	7.00	95.2
1:15	0.130	2.63	7.31	95.1
1:21	0.132	2.52	7.18	94.8
1:27	0.169	2.45	5.51	93.1

[a] The lifetime for the shorter of the trace at 658 nm. [b] The lifetime for the longer of the trace at 658 nm. [c] Intermolecular triplet state energy transfer rate constant. [d] Intermolecular triplet state energy transfer efficiency.

6. x,y,z coordinates of the optimized geometries

DFT calculation at b3lyp/genecp level.

Pd-Pc

0 1

C	2.54837700	0.98670900	0.01020400
C	2.56702700	-1.35899500	-0.00207200
N	1.19821800	1.21818500	-0.00472600
N	1.22160000	-1.61176600	-0.01197900
C	0.94532800	2.56509000	-0.00703900
C	2.28154000	-3.64648800	-0.01834000
C	0.99010900	-2.96337800	-0.02253200
N	-1.63156700	1.19566100	-0.04643400
N	-1.60892400	-1.63498600	-0.05323100
C	-1.40037700	2.54537000	-0.03671500
C	-2.97885000	0.94260900	-0.06104400
C	-1.35613500	-2.98188900	-0.04984600
C	-2.95899500	-1.40354500	-0.06878000
C	-2.69253400	3.22668000	-0.04432000
C	-3.68294400	2.22281300	-0.06014500
C	-2.63585100	-3.68590900	-0.06444600
C	-3.64000200	-2.69554000	-0.07631800
C	-4.99064200	-3.03520000	-0.09715700
H	-5.77134600	-2.28326200	-0.12323900
C	-2.95432600	-5.04437900	-0.07468100
H	-2.17816200	-5.80220200	-0.07495400
C	-5.29365000	-4.39701400	-0.09927800
C	-4.30278300	-5.39633900	-0.09304900
H	-4.59858600	-6.43952300	-0.11843400
C	-5.04111900	2.54142800	-0.07674800
C	-3.03165600	4.57740100	-0.04227000
C	-4.39355100	4.88073700	-0.04985400
C	-5.39278100	3.89034000	-0.07182500
H	-6.43565000	4.18698400	-0.09997000
H	-5.79898200	1.76561000	-0.09872100
H	-2.27924000	5.35807800	-0.04627400
C	3.89224900	4.97961400	0.04044200
H	4.18821400	6.02270400	0.06619900
C	4.88290300	3.98065500	0.04814200
C	4.57999600	2.61849000	0.04374100

H	5.36039300	1.86619400	0.07011300
C	2.54342300	4.62767100	0.01980600
H	1.76720900	5.38543600	0.01854000
C	2.22564400	3.26944200	0.00862500
C	3.22960800	2.27928200	0.02020600
C	3.26939400	-2.63998600	-0.00670400
C	4.62542500	-2.95734300	-0.01313700
H	5.39334000	-2.19187500	-0.02408500
C	4.95062200	-4.31428300	-0.02331700
C	3.97630600	-5.32921500	-0.03776000
H	4.29017900	-6.36690400	-0.06748300
C	2.62190800	-4.99922400	-0.03519200
H	1.85821000	-5.76938500	-0.05329500
N	-0.17758000	-3.59031900	-0.03683400
N	-3.58668200	-0.23538600	-0.07161100
N	-0.23246000	3.17344700	-0.01983900
N	3.17596900	-0.18073800	0.01040700
Pd	-0.20531800	-0.20837400	-0.02847800
S	-7.02413000	-4.89504700	-0.12471700
O	-7.80803300	-3.78098700	-0.69116300
O	-7.10206700	-6.23277800	-0.74210000
C	-7.46537500	-5.05808600	1.61696900
H	-8.51317300	-5.36805900	1.64411900
H	-6.83130600	-5.81799400	2.07731500
H	-7.34050900	-4.09181100	2.10917400
S	-4.89075000	6.61178600	-0.04128400
S	6.61359200	4.47880200	0.08056900
S	6.68946200	-4.78413900	-0.03588100
O	-3.77771100	7.40548800	-0.59605500
O	-6.23023200	6.70248100	-0.65297400
O	6.68634900	5.82434500	0.68148400
O	7.39196800	3.37222800	0.66877300
O	7.45439400	-3.67247600	-0.63196000
O	6.78921000	-6.13600600	-0.61846000
C	-5.04796000	7.01949300	1.70909600
H	-5.35390500	8.06769500	1.75739200
H	-5.80930900	6.37934800	2.15854600
H	-4.08106600	6.88149400	2.19660100
C	7.06863300	4.61856100	-1.65942700
H	6.43908500	5.37329000	-2.13429600
H	8.11706200	4.92672400	-1.68239800
H	6.94630200	3.64614400	-2.14004100
C	7.13329500	-4.89373800	1.70918300
H	6.51450700	-5.65450300	2.18850000
H	8.18716900	-5.18147400	1.74386000
H	6.98881200	-3.91797200	2.17665300

Pt-Pc

0 1

C	2.56522600	1.00161000	0.00387500
C	2.58480300	-1.34434700	-0.01103400
N	1.21099100	1.23114100	-0.00659100
N	1.23547000	-1.59628700	-0.01560900
C	0.95867700	2.58191900	-0.00209300
C	2.29718600	-3.63169500	-0.02321000
C	1.00572200	-2.95196500	-0.02262300
N	-1.61674700	1.20752100	-0.02528600
N	-1.59308300	-1.62066200	-0.03259400
C	-1.38751900	2.56144500	-0.01978000
C	-2.96778500	0.95517900	-0.03927800
C	-1.34094300	-2.97139900	-0.03560500
C	-2.94729900	-1.39119300	-0.04611300
C	-2.67997900	3.23912400	-0.02911600
C	-3.66941500	2.23481600	-0.04348900
C	-2.62021700	-3.67306200	-0.05035400
C	-3.62476500	-2.68346200	-0.05723500
C	-4.97509200	-3.02402500	-0.08109100
H	-5.75626000	-2.27251300	-0.10436700
C	-2.93802600	-5.03161100	-0.06800100
H	-2.16125500	-5.78879000	-0.07238100
C	-5.27756600	-4.38594900	-0.09178800
C	-4.28613000	-5.38456200	-0.08999300
H	-4.58070800	-6.42789200	-0.12247100
C	-5.02783300	2.55250600	-0.06818000
C	-3.02044400	4.58970400	-0.03381600
C	-4.38215800	4.89218000	-0.05188700
C	-5.38068200	3.90081800	-0.07500100
H	-6.42420200	4.19415700	-0.11426400
H	-5.78480300	1.77583300	-0.09014300
H	-2.26973600	5.37188300	-0.03677600
C	3.90429400	4.99497500	0.05261300
H	4.19939200	6.03812100	0.08453200
C	4.89547100	3.99667600	0.05441100
C	4.59303100	2.63442500	0.04199100
H	5.37376900	1.88236900	0.06432200
C	2.55577500	4.64212100	0.03083400
H	1.77900600	5.39930100	0.03485600
C	2.23851000	3.28382500	0.01271200
C	3.24291000	2.29434200	0.01745500
C	3.28463200	-2.62509500	-0.01688800
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H	5.40830600	-2.17674300	-0.04065900
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H	4.30609500	-6.35205900	-0.07290200
C	2.63801600	-4.98433400	-0.03856400
H	1.87431700	-5.75457300	-0.05261200
N	-0.16198600	-3.57573000	-0.03016900
N	-3.57176100	-0.22323400	-0.04834100
N	-0.21961900	3.18617200	-0.00794900
N	3.18970500	-0.16579000	0.00001400
S	-7.00754400	-4.88454600	-0.12707300
O	-7.79099100	-3.76314000	-0.67953200
O	-7.08329600	-6.21350300	-0.76343700
C	-7.45304100	-5.07264000	1.61091700
H	-8.50061900	-5.38397100	1.63079800
H	-6.81957400	-5.83842100	2.06225800
H	-7.33051700	-4.11334400	2.11711400
S	-4.87969700	6.62288800	-0.06364300
S	6.62570900	4.49532000	0.09263000
S	6.70518200	-4.76844400	-0.04877800
O	-3.73165300	7.42063800	-0.53496200
O	-6.17398100	6.71809900	-0.76560100
O	6.69674800	5.83709600	0.70214700
O	7.40357800	3.38546800	0.67539200
O	7.46948000	-3.65645800	-0.64510500
O	6.80505000	-6.12018000	-0.63166900
C	-5.15830000	7.01804700	1.67418300
H	-5.46920100	8.06539200	1.70815300
H	-5.94737100	6.37385600	2.06645000
H	-4.22687800	6.87843500	2.22584900
C	7.08459500	4.64628500	-1.64538100
H	6.45620700	5.40409800	-2.11685100
H	8.13310500	4.95451000	-1.66394700
H	6.96338300	3.67699800	-2.13254700
C	7.15011600	-4.87833800	1.69602700
H	6.53158400	-5.63918200	2.17555900
H	8.20401000	-5.16606900	1.73012200
H	7.00580900	-3.90265300	2.16372200
Pt	-0.19102000	-0.19475400	-0.01897200

7. Calculation details

Table S2. Excitation Energies (eV) and corresponding Oscillator Strengths (*f*), main configurations and CI coefficients of the Low-lying Electronically Excited States of complex **Pt-Pc**. Calculated by TDDFT//B3LYP/LANL2DZ, based on the DFT//B3LYP/LANL2DZ Optimized Ground State Geometries.

	TDDFT/B3LYP/LANL2DZ					
	Electronic transition	Energy [eV/nm] [a]	*f* [b]	Composition [c]	CI [d]	Character
Singlet	$S_0 \rightarrow S_1$	2.08 / 596	0.6825	H→L	0.6984	LMCT
	$S_0 \rightarrow S_2$	2.11 / 588	0.7146	H→L+1	0.6981	LMCT
	$S_0 \rightarrow S_{16}$	3.76 / 329	0.4506	H-5→L+1	0.4474	LMCT
Triplet	$S_0 \rightarrow T_1$	1.33 / 930	0.0000[e]	H→L	0.7063	LMCT
	$S_0 \rightarrow T_2$	1.35 / 916	0.0000[e]	H→L+1	0.7058	LMCT
	$S_0 \rightarrow T_3$	2.38 / 520	0.0000[e]	H-2→L	0.5084	ILCT
	$S_0 \rightarrow T_4$	2.46 / 504	0.0000[e]	H-1→L+1	0.5210	ILCT
	$S_0 \rightarrow T_5$	2.49 / 499	0.0000[e]	H-1→L	0.6250	ILCT

[a] Only the selected low-lying excited states are presented. [b] Oscillator strengths. [c] Only the main configurations are presented. [d] The CI coefficients are in absolute values. [e] No spin-orbital coupling effect was considered, thus the *f* values are zero.

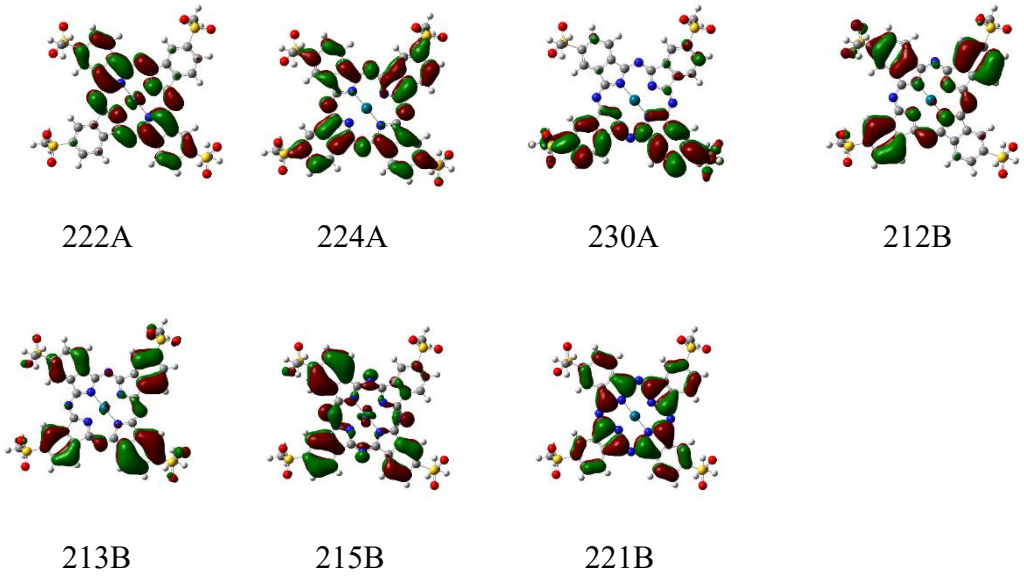

Fig. S10. Selected frontier molecular orbitals of the triplet state of **Pd-Pc** (in chloroform).

Table S3. Electronic Excitation Energies (eV) and corresponding Oscillator Strengths (f), main configurations and CI coefficients of the Low-lying Electronically Triplet Excited States of **Pd-Pc** calculated by TDDFT//B3LYP/6-31G(d), based on the DFT//B3LYP/6-31G(d) Optimized T_1 Excited State Geometries

	TDDFT/B3LYP/LANL2DZ				
	Electronic transition	Energy [eV/nm] [a]	*f* [b]	Composition	CI [c]
Triplet	$T_1 \rightarrow T_4$	1.80 / 690	0.2678	222A→224A	0.8997
	$T_1 \rightarrow T_{12}$	2.28 / 543	0.1548	215B→221B	0.7019
	$T_1 \rightarrow T_{15}$	2.35 / 528	0.1505	213B→221B	0.6376
	$T_1 \rightarrow T_{17}$	2.48 / 499	0.5746	212B→221B	0.7051
	$T_1 \rightarrow T_{45}$	3.38 / 367	0.1400	222A→230A	0.7244

[a] Only the selected low-lying excited states are presented. [b] Oscillator strength. No spin-orbital coupling effect was considered in the calculation thus the oscillators are zero. [c] The CI coefficients are in absolute values.

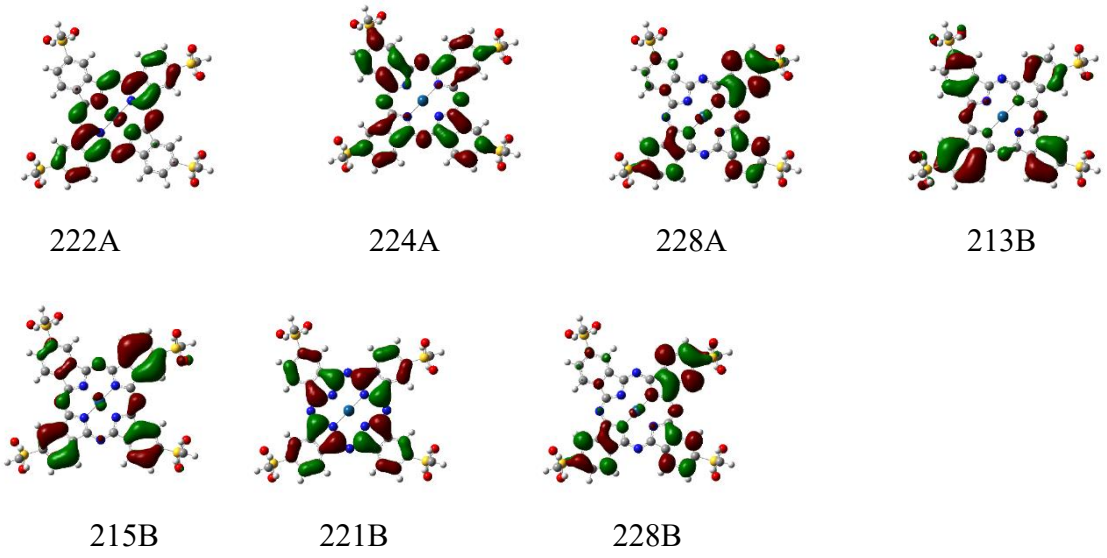

Figure S15. Selected frontier molecular orbitals of the triplet state of **Pd-Pc** (in chloroform).

Table S4. Electronic Excitation Energies (eV) and corresponding Oscillator Strengths (f), main configurations and CI coefficients of the Low-lying Electronically Triplet Excited States of **Pt–Pc** calculated by TDDFT//B3LYP/6-31G(d), based on the DFT//B3LYP/6-31G(d) Optimized T_1 Excited State Geometries

	TDDFT/B3LYP/LANL2DZ				
	Electronic transition	Energy [eV/nm] [a]	f [b]	Composition	CI[c]
Triplet	$T_1 \rightarrow T_5$	1.72 / 723	0.2327	222A→224A	0.9426
	$T_1 \rightarrow T_{11}$	2.25 / 551	0.1871	215B→221B	0.3532
	$T_1 \rightarrow T_{14}$	2.31 / 537	0.1815	213B→221B	0.5938
	$T_1 \rightarrow T_{16}$	2.45 / 505	0.3196	222A→228B	0.5202
	$T_1 \rightarrow T_{17}$	2.46 / 504	0.3293	222A→228A	0.5311

[a] Only the selected low-lying excited states are presented. [b] Oscillator strength. No spin-orbital coupling effect was considered in the calculation thus the oscillators are zero. [c] The CI coefficients are in absolute values.