Supporting information for

Accessing the Long-lived Near-IR-Emissive Triplet Excited State in Naphthalenediimide With Light-harvesting Diimine Platinum(II) Bisacetylide Complex and Its Application for Upconversion

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General.

All the chemicals used in synthesis are analytical pure and were used as received. Solvents were dried and distilled. NMR spectra were recorded on a 400 MHz Varian Unity Inova NMR spectrophotometer. ^{13}C NMR spectra were recorded on the same instrument (100 MHz) with total proton decoupling. Mass spectra were recorded with Q-TOF Micro MS spectrometer. UV-Vis absorption spectra were measured with a HP8453 UV-visible spectrophotometer. Fluorescence spectra were recorded on JASCO FP-6500 or a Sanco 970 CRT spectrofluorometer. Fluorescence/phosphorescence lifetimes were measured on a Horiba Jobin Yvon Fluoro Max-4 (TCSPC) instrument. The nanosecond time-resolved transient difference absorption spectra were detected by Edinburgh LP900 instruments (Edinburgh Instruments, U.K.). The signal was buffered on a Tektronix TDS 3012B oscilloscope and was analysized by the LP900 software. All samples in flash photolysis experiments were deaerated with argon for ca. 15 min before measurement and the gas flow is kept during the measurement.

Diode pumped solid state laser (DPSSL) with 532 nm were used as excitation source for the upconversion experiments. The diameter of the laser spot is ca. 3 mm. The output power of the DPSS laser can be adjusted continuously. The laser power was measured with phototube. For 532 nm laser, the variation of the power is less than ±5% over eight hours. The noise of the 532 nm DPSS laser is 20%-25% in the range of 1 kHz- 1 MHz.

For the upconversion experiments, the mixed solution of the complex (triplet sensitizer) and perylene (triplet acceptor) was degassed for at least 15 min with N_2 or Ar. Then the solution was excited with laser. The upconverted fluorescence of perylene was observed with fluorospectrometer. The upconversion quantum yields were calculated with the following equation, where Φ_{UC}, A_{unk}, I_{unk} and η_{unk} represents the quantum yield, absorbance, integrated photoluminescence intensity and the refractive index of the samples and the solvents (**Eq. 1**). The equation is multiplied by factor 2 in order to made the maximum quantum yield to be unit.[1]

$$\Phi_{UC} = 2\Phi_{std}\left(\frac{A_{std}}{A_{unk}}\right)\left(\frac{I_{unk}}{I_{std}}\right)\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2 \qquad \textbf{(Eq. 1)}$$

The density functional theory (DFT) calculations were used for optimization of the ground state geometries, for both singlet states and triplet states. The energy level of the T_1 state of the acetylide ligand **5** (energy gap between S_0 state and T_1 state) were calculated with the time-dependent DFT (TDDFT), based on the optimized singlet state geometries. The spin density surfaces of the complexes were calculated based on the optimized triplet state geometries. All the calculations were performed with Gaussian 09.[2]

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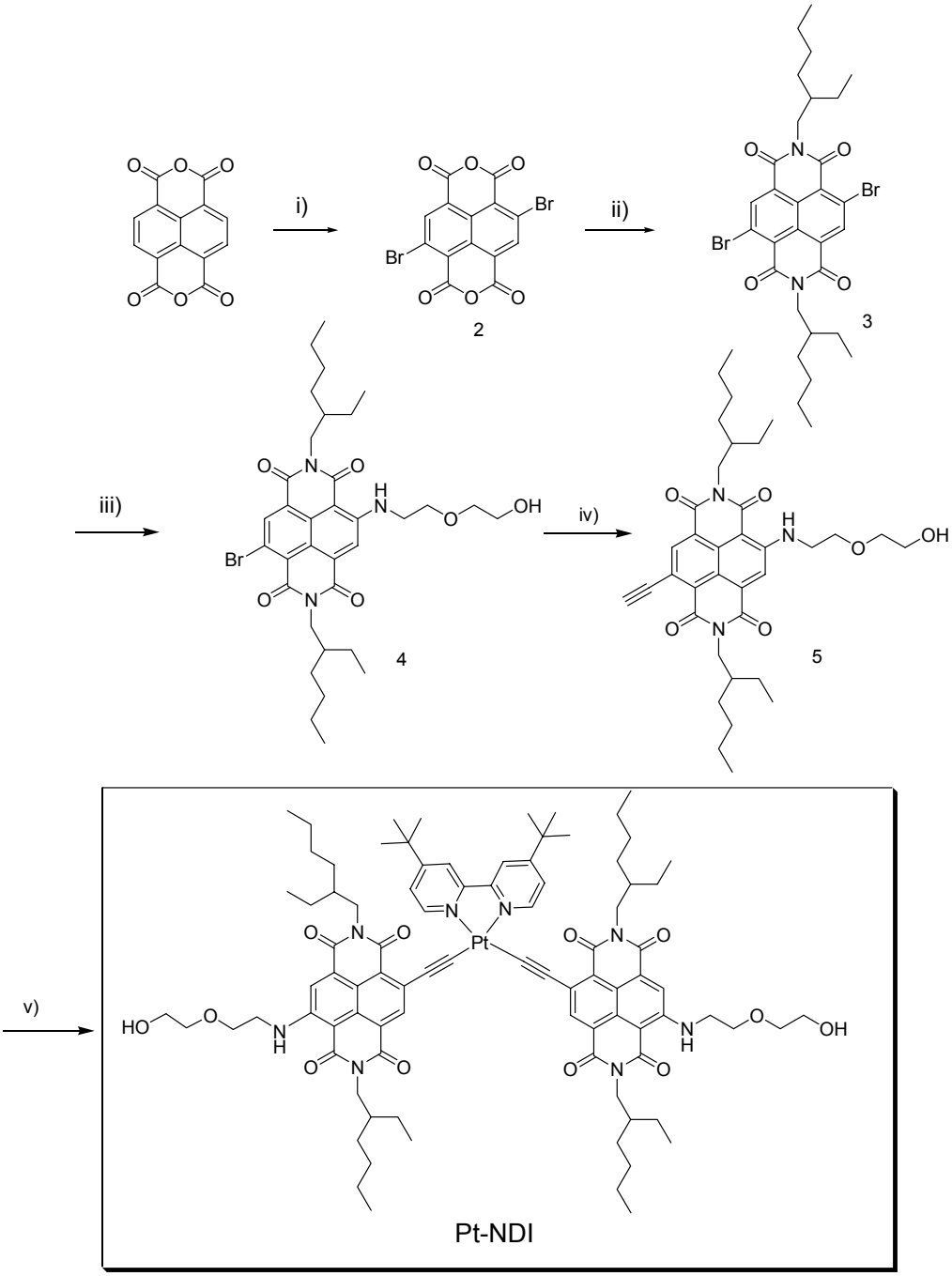
(1). Singh-Rachford, T. N.; Castellano, F. N. *Coord. Chem. Rev.* **2010**, *254*, 2560–2573.

(2). Frisch, M. J.; Trucks, G. W.; Schlegel, H. B. et al. *Gaussian 09 Revision A.1*, Gaussian Inc., Wallingford CT, **2009**.

Experimental Section

Synthesis:



Scheme 1. Synthesis route of target donors 1. i) DBI, oleum, 85 °C, 43 h, 82.2 %; ii) 2-ethyl-hexylamine, acetic acid, 120 °C, 5 h, 52 %; iii) DGA, 2-methoxyethanol, 120 °C, 8 h, 71 %; iv) $Pd(PPh_3)_4$, CuI, NEt_3,ethynyltrimethylsilane, argon atmosphere, 40 °C, 4 h, then CH_2Cl_2, methanol, K_2CO_3, room temperature, 5 h, 36.8 %; v) CH_2Cl_2, i-Pr_2NH, room temperature, 24 h.

2,6-dibromonaphthalene-1,4,5,8-tetracarboxydianhydride (2)

2,6-dibromonaphthalene-1,4,5,8-tetracarboxydianhydride was synthesized according to a literature procedure.[3]

(3). Chen, Z.; Zheng, Y.; Yan, H.; Facchetti, A. *J. Am.Chem. Soc.*, **2009**, *131*, 8–9.

***N,N'*-Di-(2-ethylhexan-1-amine)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxydianhydride (3)**

The mixture of compound **2** (2.13 g, 5 mmol), 2-ethylhexan-1-amine (2.71 g, 21 mmol), and acetic acid (150 mL) was refluxed for 5 h. After having been cooled to room temperature, the precipitate was filtered and washed with water(300 mL). Then the residue was purified with column chromatography (silica gel; dichloromethane /n-hexane, 2:1, V/V) to give 1.68 g (yield: 52.0 %) of an orange crystal. ^{1}H NMR (400 M Hz, $CDCl_3/CD_3OD$) δ 8.99 (s,2H), 4.11–4.20 (m, 4H), 1.93–1.96 (m, 2H), 1.25–1.43 (m, 16H), 0.94 (t, 6H, *J*=7.2 Hz), 0.89 (t, 6H, *J*=7.2 Hz). ESI-HRMS ($[C_{30}H_{36}N_2O_4Br_2]^+$): calcd 648.1021, found 648.1005.

***N,N'*-Di-(2-ethylhexan-1-amine)-2-(Diethyleneglycolamino)-6-bromonaphthalene-1,4,5,8-tetracarboxydianhydride (4)**

The mixture of compound **3** (500.0 mg, 0.75 mmol), 2-(2-aminoethoxy)ethanol (125.0 mg, 1.2 mmol), and methoxyethanol (20 mL) was stirred at 120 °C for 8 h. After removal of methoxyethanol in vacuum, the residue was purified with column chromatography (silica gel; dichloromethane /methanol, 100:1, V/V) to give 358 mg (yield: 71.0 %) of a red solid. 1H NMR (400 M Hz, $CDCl_3/CD_3OD$) δ 10.35 (s, 1H), 8.78 (d, 1H, *J*=3.2 Hz), 8.34 (d,1H, *J*=3.2 Hz), 4.03-4.16 (m, 4H), 3.90 (t, 2H, *J*=4.8 Hz),3.80 (d, 4H, *J*=4.8 Hz), 3.70 (t, 2H, *J*=4.8 Hz), 1.87-1.93 (m, 2H), 1.25-1.38 (m, 16H), 0.93 (t, 6H, *J*=7.2 Hz), 0.88 (t, 6H, *J*=7.2 Hz). ESI-HRMS ($[C_{34}H_{46}N_3O_6Br + Na]^+$): calcd 694.2447, found 694.2439.

***N,N'*-Di-(2-ethylhexan-1-amine)-2-(Diethyleneglycolamino)-6-ethynylnaphthalene-1,4,5,8-tetracarboxydianhydride (5)**

Compound 4 (160.0 mg, 0.24 mmol), PPh_3(25.4 mg, 0.0096mmol) and $Pd(PPh_3)_2$ Cl_2(33.4 mg, 0.0048 mmol) were dissolved in 10 mL of triethylamine under a argon atmosphere. Ethynyltrimethylsilane (0.8ml) was added to the above solution and CuI (20.2 mg, 0.0096 mmol) was added then. The mixture was stirred at 40 °C for 4 h. After removal of triethylamine in vacuum, the residue was purified with column chromatography (silica gel; dichloromethane /methanol, 100:1, V/V) to give some red solid. The red solid was dissolved in 15 ml of mixed solvent (dichloromethane /methanol, 2:1, V/V), then K_2CO_3(1g, 7.23mmol) was added. The mixture was stirred at room temperature for 5 h. The precipitate was filtered and washed with water(30ml). Then the residue was purified with column chromatography (silica gel; dichloromethane /methanol, 35:1, V/V) to give 54.5mg (yield: 36.8 %) of an red solid. ^{1}H NMR (400 M Hz, $CDCl_3/CD_3OD$) δ 10.44 (t, 1H, J=6.0 Hz), 8.74 (s,1H), 8.38 (s,1H), 4.07-4.14 (m, 4H), 3.89 (t, 2H, *J*=4.8 Hz), 3.79-3.83 (m, 4H), 3.76 (S, 1H), 3.69 (t, 2H, *J* = 4.8 Hz), 1.87-1.99 (m, 2H), 1.29-1.39 (m, 16H), 0.92 (t, 6H, *J*=7.2 Hz), 0.88 (t, 6H, *J*=7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3/CD_3OD$) δ 166.5, 163.0, 162.6, 162.3, 152.5, 138.2, 129.0, 127.5, 126.4, 122.8, 121.2, 120.0, 119.6, 100.2, 86.0, 82.3, 72.9, 69.6, 62.0, 53.4, 44.9, 44.1, 43.0, 37.8, 37.7, 30.7, 30.6, 28.6, 28.6, 24.0, 23.9, 23.1, 23.1, 14.1, 10.7, 10.6. ESI-HRMS ($[C_{36}H_{47}N_3O_6 + Na]^+$): calcd 640.3363, found 640.3349.

Pt-NDI

Compound **5** (100.0 mg, 0.16 mmol) and Pt(dbbpy) Cl_2(23.0 mg, 0.0044 mmol) were dissolved in 10 mL of dichloromethane under a argon atmosphere. Diisopropylamine (2ml) was added to the above solution and CuI (5.0 mg, 0.0024 mmol) was added then. The mixture was stirred at 25 °C for 24 h. After removal of solvent in vacuo, the residue was purified with column chromatography (silica gel; dichloromethane /methanol, 15:1, V/V) to give some purple solid. ^{1}H NMR (400 M Hz, $CDCl_3/CD_3OD$) δ 10.49 (d, 2H, *J* = 6.0 Hz), 10.20 (t, 2H, *J* = 4.8 Hz), 9.01 (s, 2H), 8.36 (s, 2H), 7.99 (s, 2H), 7.65 (d, 2H, *J* = 6.0 Hz), 4.06-4.24 (m, 8H), 3.88 (t, 4H, *J*=4.8 Hz), 3.80 (t, 8H, *J*=4.8 Hz), 3.69 (t, 4H, *J* = 4.8 Hz), 2.88 (t,2H, *J* = 4.8 Hz), 2.04-2.10 (m, 2H), 1.91-1.97 (m, 2H), 1.48 (s, 18H), 1.25-1.44 (m, 32H), 0.89-0.96 (m, 12H), 0.81-0.88 (m, 12H). ESI-HRMS ($[C_{90}H_{116}N_8O_{12}Pt + H]^+$): calcd 1697.8472, found 1697.8331. Anal. Calcd. For $C_{90}H_{116}N_8O_{12}Pt$ (·3CH_3OH): C, 62.29; H, 7.20; N, 6.25; Found: C, 62.82; H, 7.28; N, 5.82.

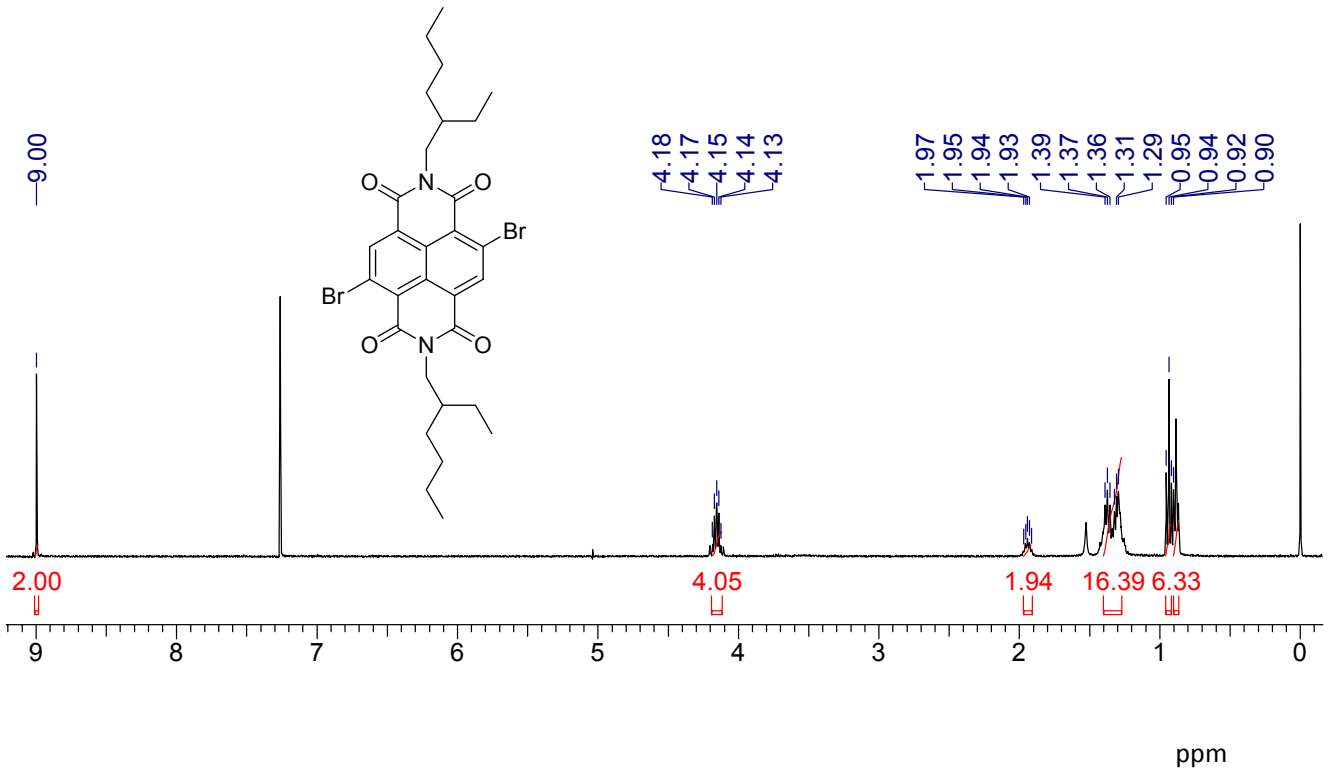


Figure S1. ^{1}H NMR of **3** ($CDCl_3$, 400 MHz).

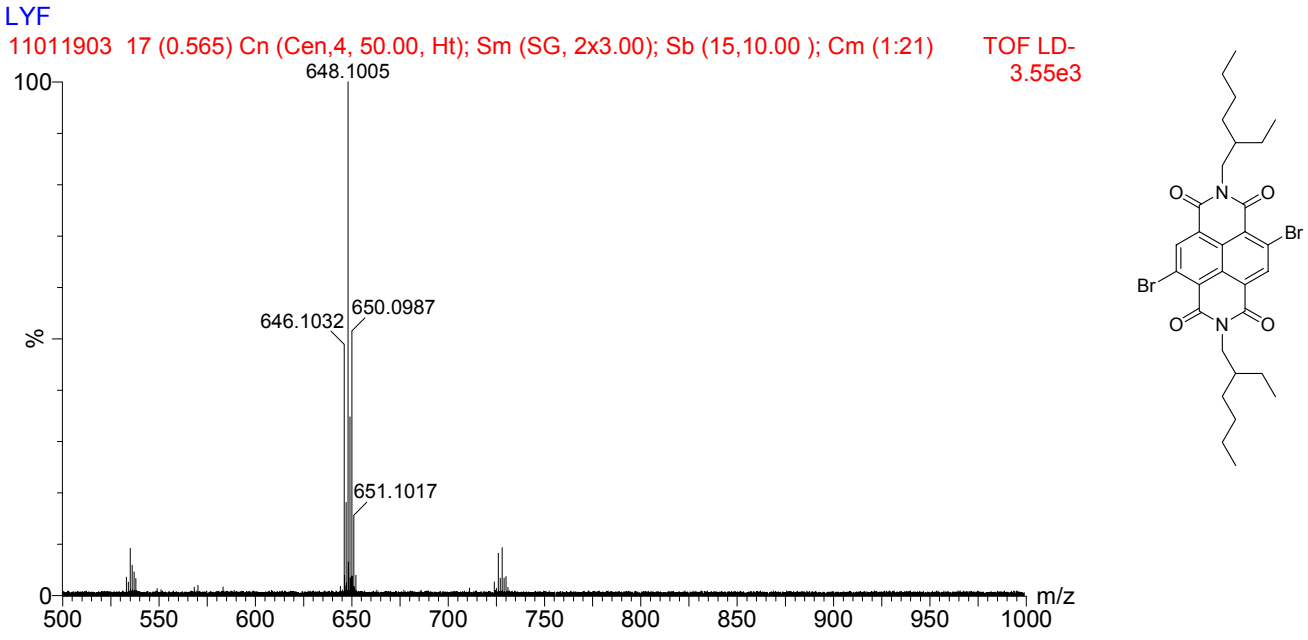


Figure S2. TOF HRMS ESI of **3**.

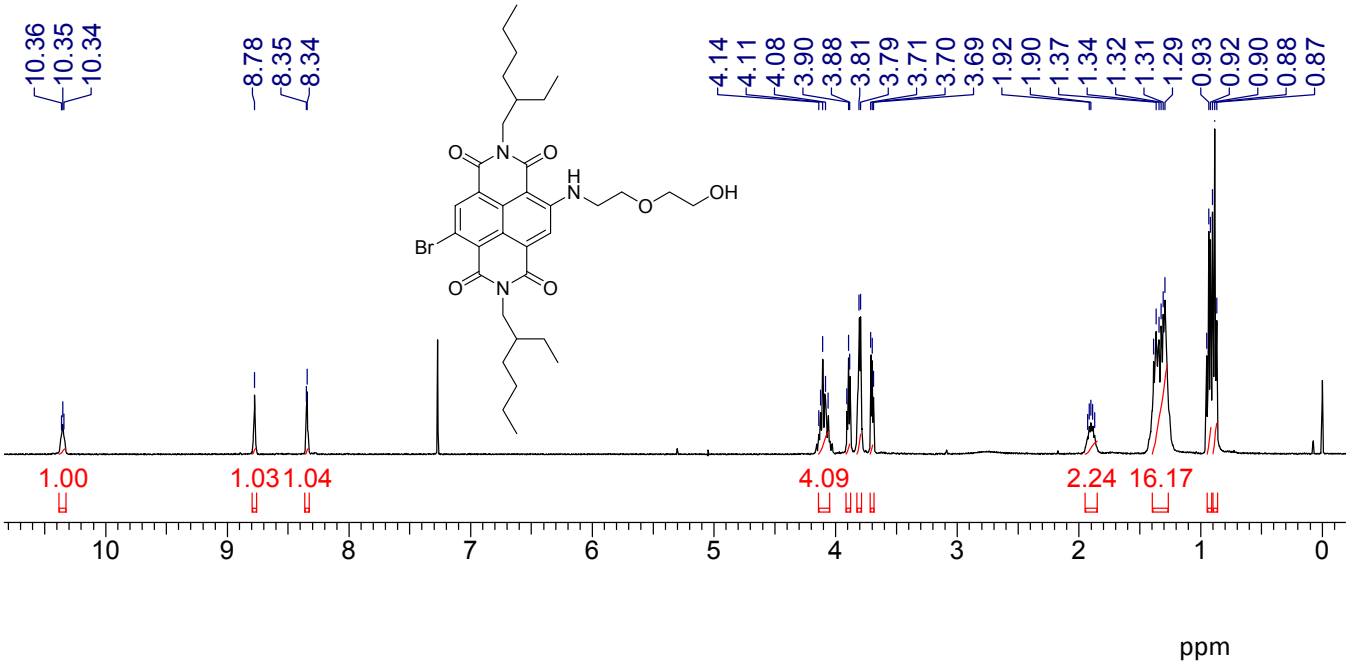


Figure S3. ^{1}H NMR of **4** ($CDCl_3$, 400 MHz).

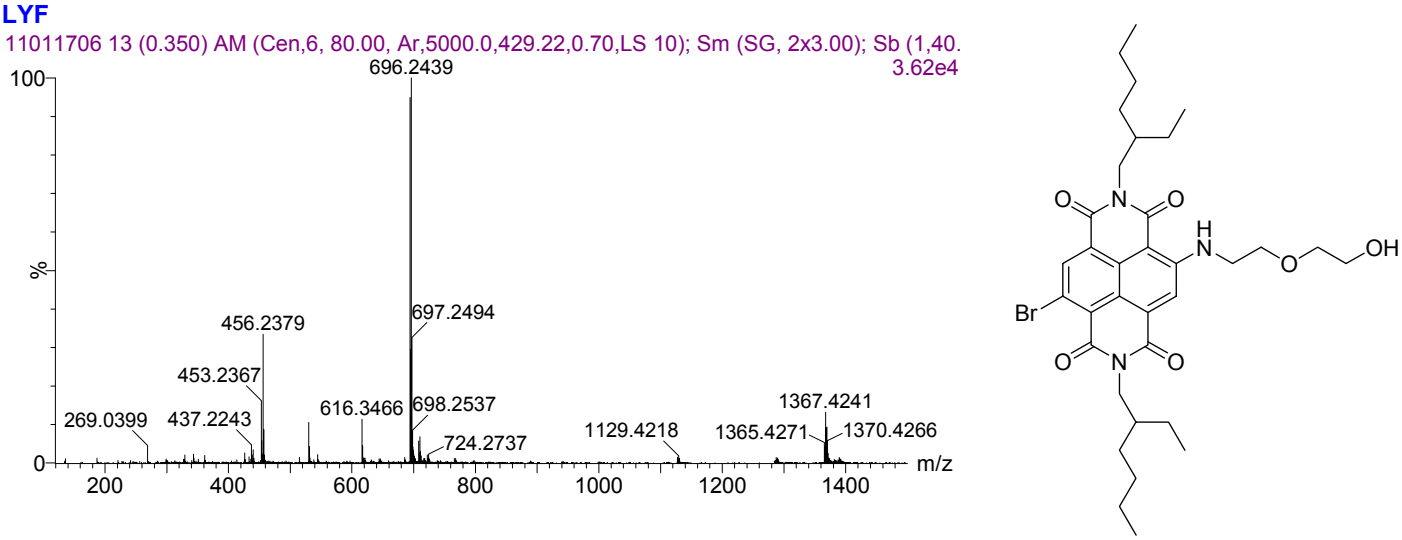


Figure S4. TOF HRMS ESI of **4**.

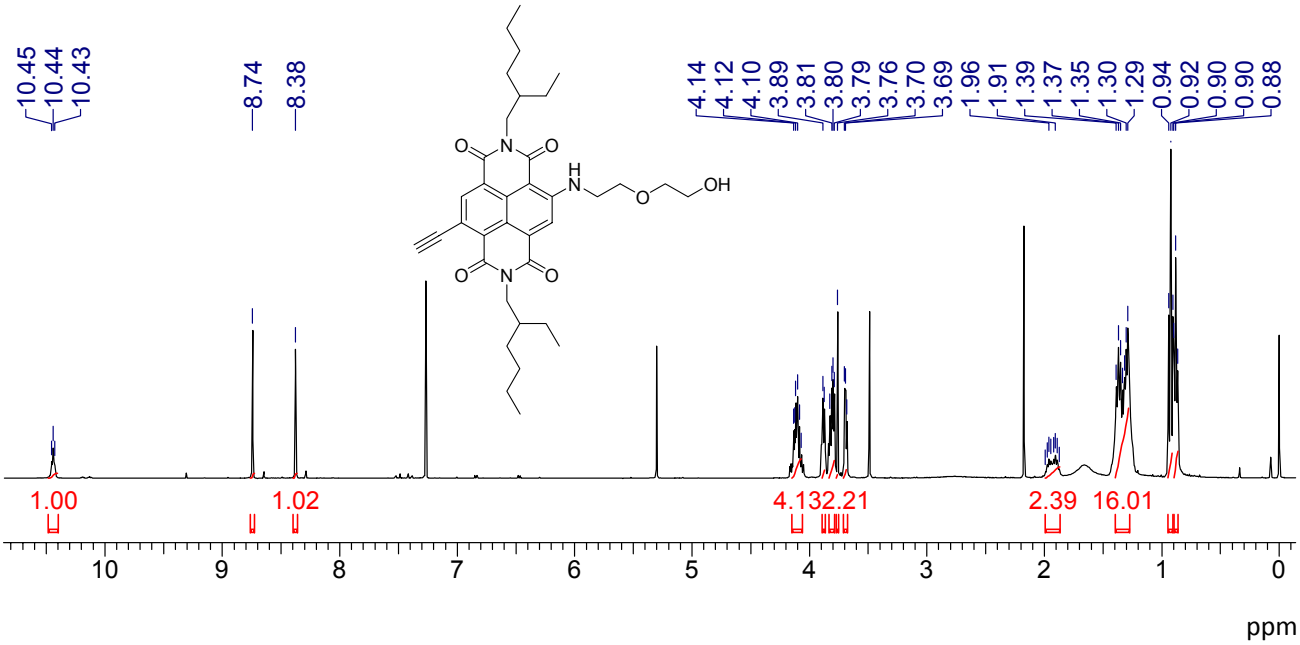


Figure S5. ^{1}H NMR of **5** ($CDCl_3$, 400 MHz).

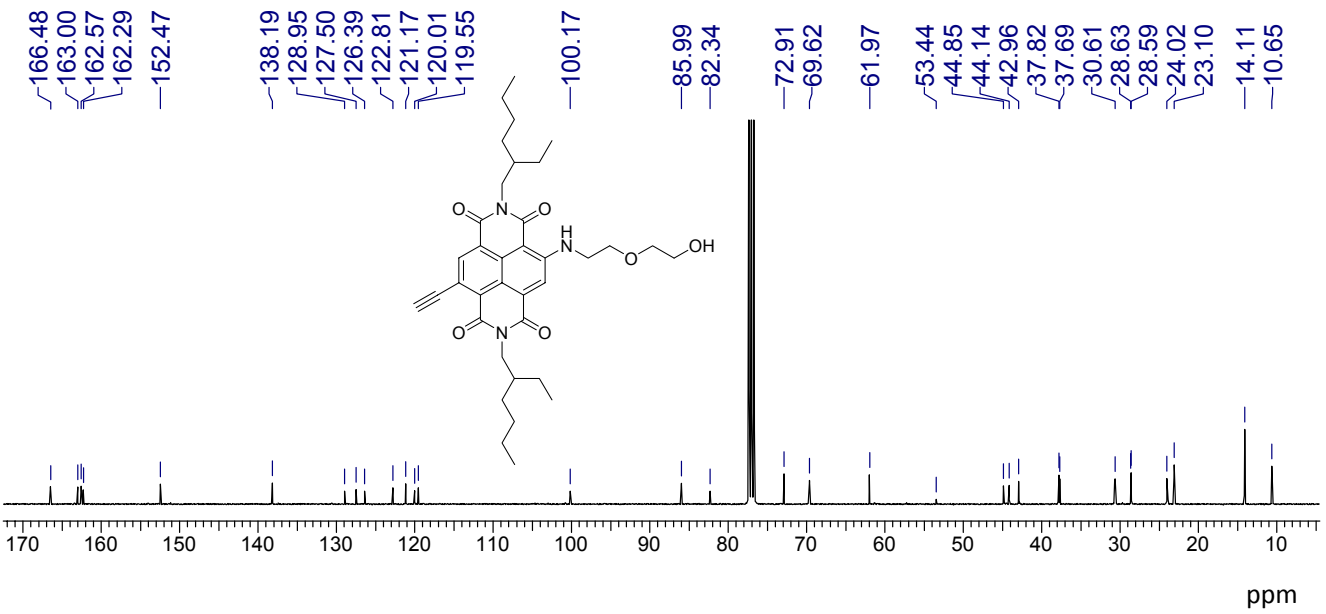


Figure S6. ^{13}C NMR of **5** ($CDCl_3$/CD_3OD, 100 MHz).

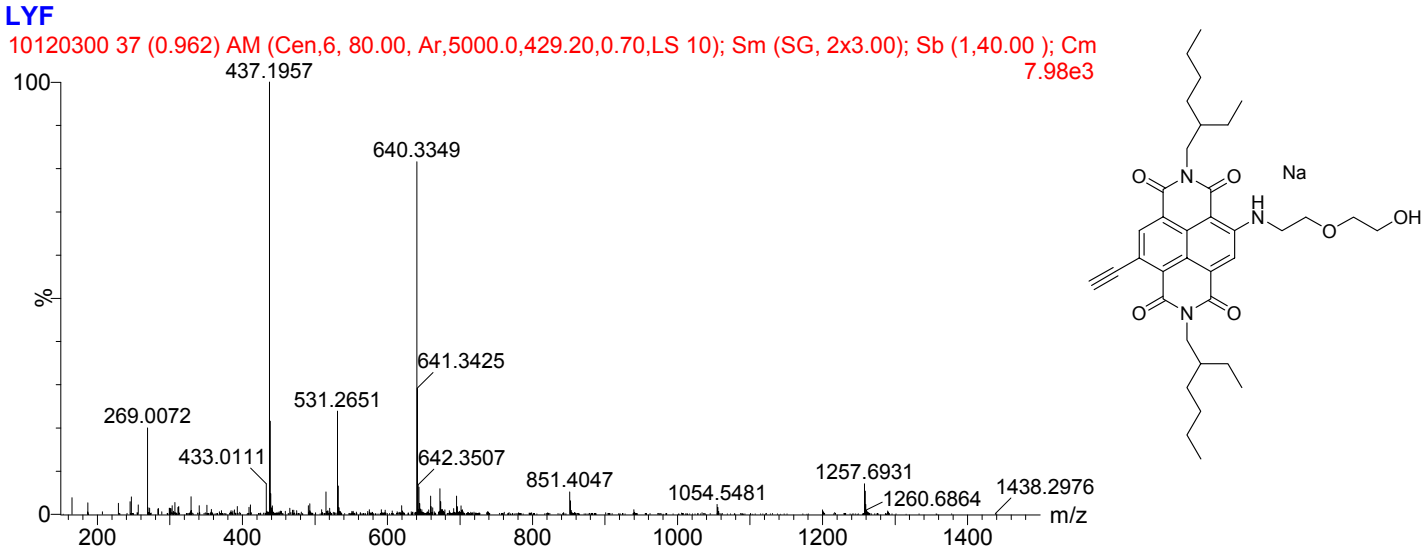


Figure S7. TOF HRMS ESI of **5**.

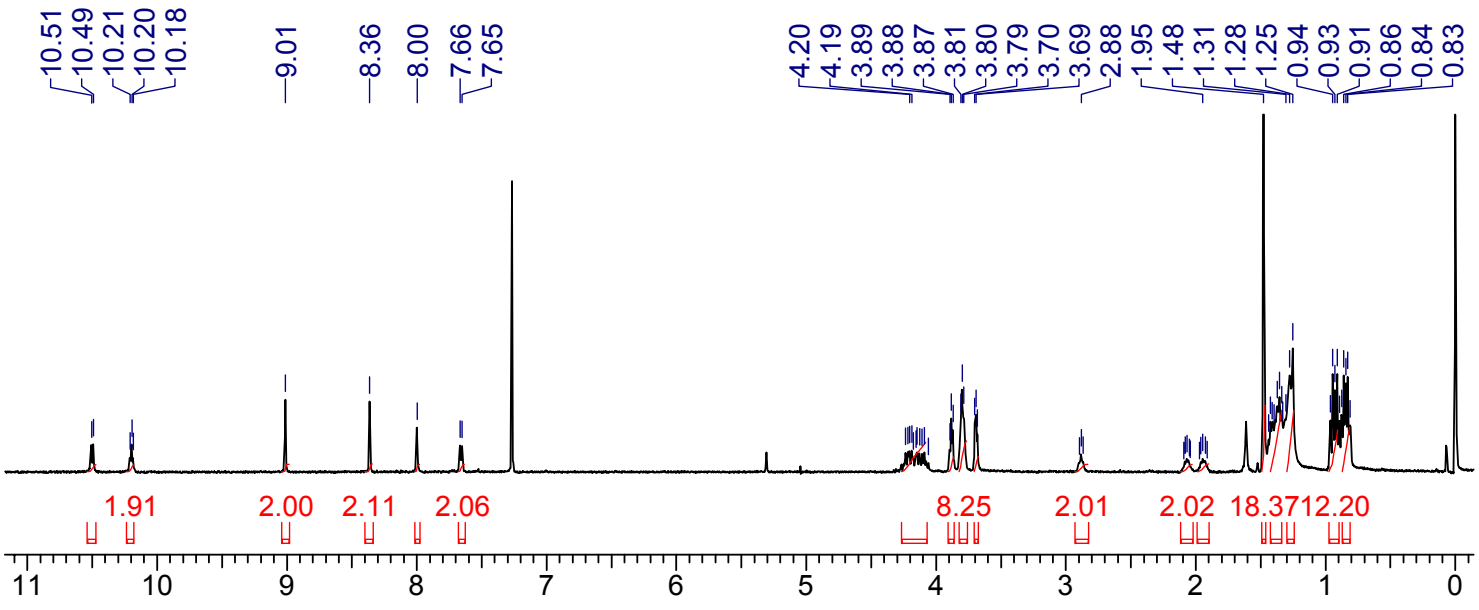
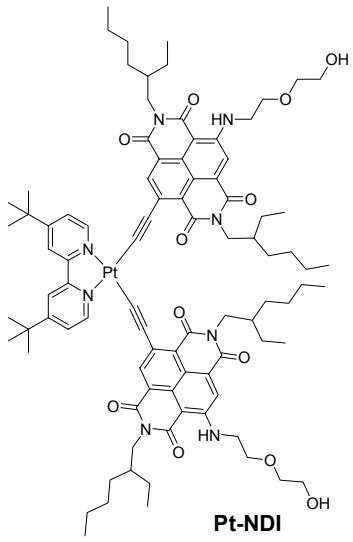


Figure S8. ^{1}H NMR of **Pt-NDI** ($CDCl_3/CD_3OD$, 100 MHz).



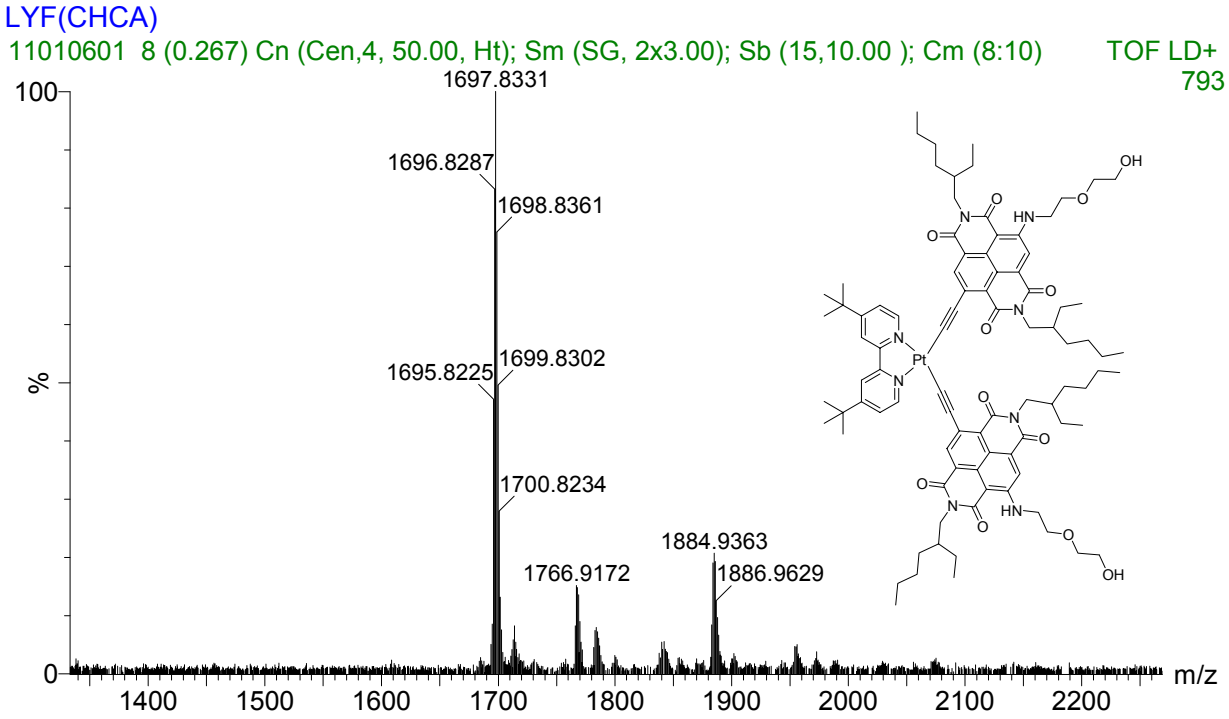


Figure S9. TOF HRMS ESI of **Pt-NDI**.

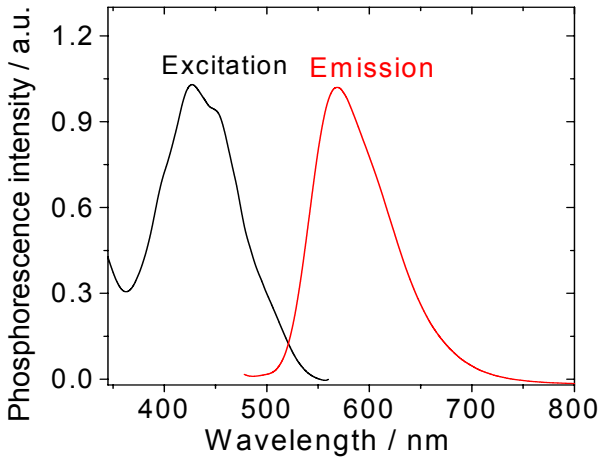


Figure S10. Excitation and Emission spectra of **Pt-Ph** in toluene, 1.0×10^{-5} M. 20 °C.

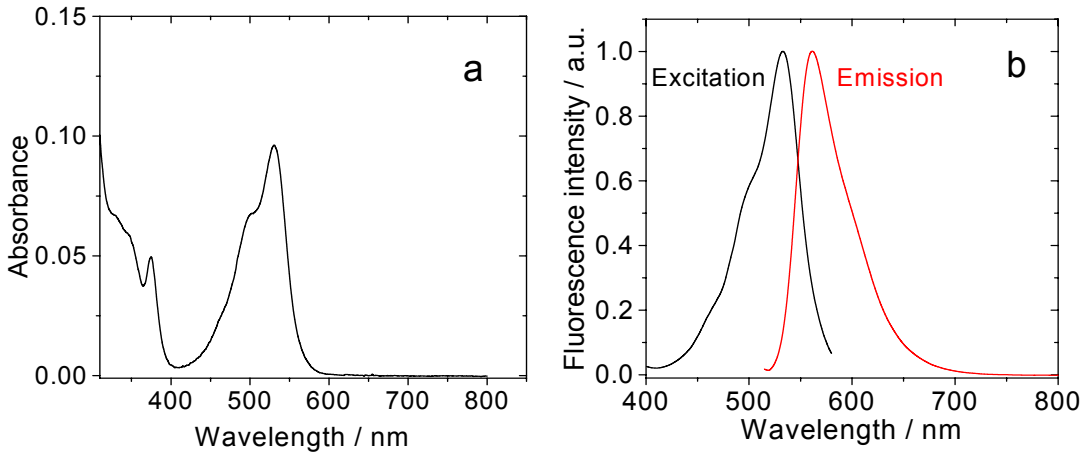


Figure S11. (a) Absorption spectra of **NDI-C≡C–H**; (b) Excitation and Emission spectra of **NDI-C≡C–H**. In toluene, 1.0×10^{-5} M. 20 °C.

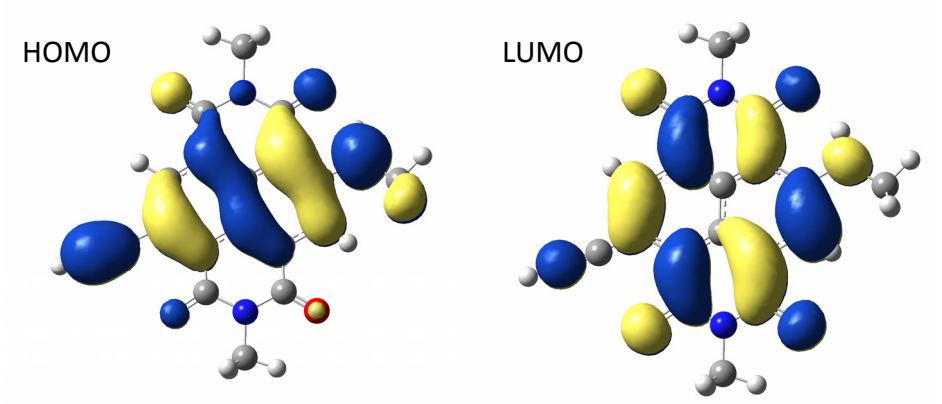


Figure S12. HOMO and LUMO of the acetylide ligand **NDI-C≡C-H**. Calculation was done with the optimized ground state geometry at B3LYP/6-31G/LANL2DZ level with Gaussian 09.

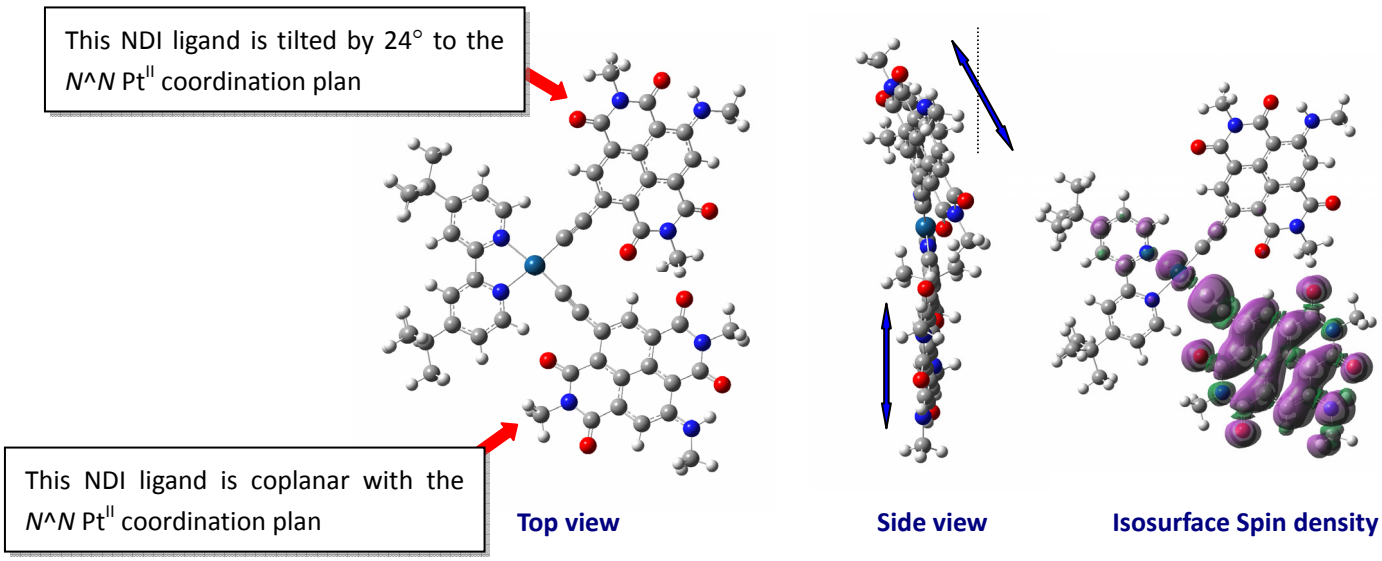
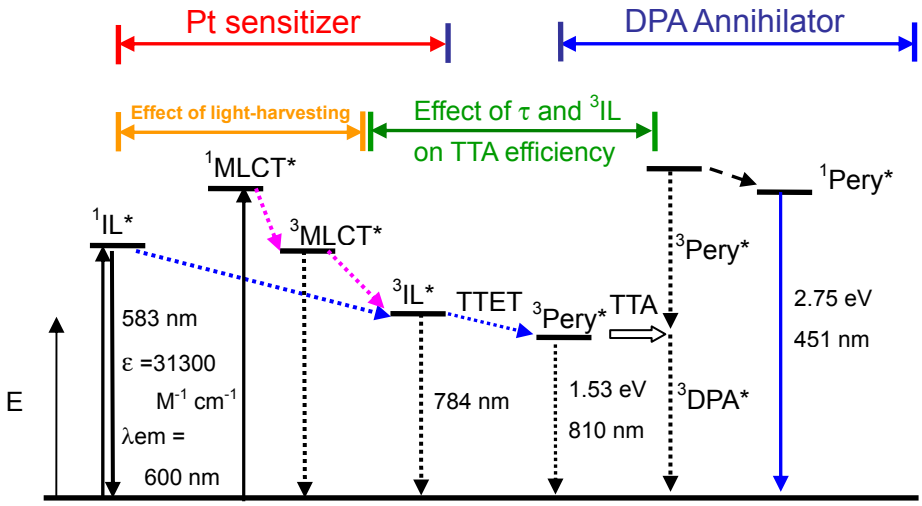


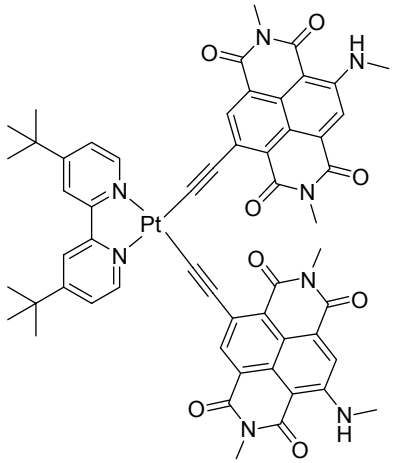
Figure S13. Optimized molecular strucuture at the T_1 state geometry and the isosurface of the spin density of **Pt-NDI** at B3LYP/6-31G/LANL2DZ level with Gaussian 09W.



Scheme S2. Qualitative Jablonski Diagram illustrating the sensitized TTA up-conversion process between **Pt-NDI** and DPA. The effect of the light-harvesting ability and the luminescence lifetime of the **Pt-NDI** sensitizer on the efficiency of the TTA-up-conversion is also shown.

E is energy. GS is ground state (S_0). ^{1}IL* is intraligand singlet excited state (coumarin localized). IC is inner conversion. ISC is intersystem crossing. ^{3}MLCT* is the Pt^{II} based metal-to-ligand-charge-transfer triplet excited state. ^{3}IL* is intraligand triplet excited state (**NDI** localized). TTET is triplet-triplet energy transfer. ^{3}DPA* is the triplet excited state of DPA. TTA is triplet-triplet annihilation. ^{1}DPA* is the singlet excited state of DPA. The emission bands observed for the sensitizers alone is the ^{3}IL emissive excited state. The emission bands observed in the TTA experiment is the simultaneous ^{3}IL* emission (phosphorescence) and the upconverted ^{1}DPA* emission (fluorescence).

Z-matrix of the optimized T_1 state geometry of the **Pt-NDI** (note the alkyl chains were simplified as methyl groups to reduce the calculation cost).



0 1

C	4.28235472	4.00761118	0.28327281
C	3.99599680	5.37733939	0.25717168
C	2.64047276	5.74003272	0.18601321
C	1.64133214	4.77369738	0.14211531
C	3.25741406	3.06628264	0.24009460
C	0.19942944	5.07515696	0.05648491
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H	5.29472742	3.63622189	0.33525707
H	3.48044533	2.00518595	0.25703515
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N	-0.62729412	3.98243293	0.01591183
N	1.95931104	3.44004477	0.17047551
Pt	0.33331340	2.11962159	0.08684645
C	-1.27918175	1.01284420	0.00225535
C	-2.26963540	0.29406962	-0.02232810
C	1.37935395	0.49101404	0.14108765
C	2.10619636	-0.50780219	0.14005681
H	0.33905392	7.20695544	0.04625221
H	2.36551015	6.78495775	0.16209916
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C	-3.81695126	8.02164075	-0.22391553
H	-4.17030567	7.51960289	-1.13129417
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H	4.01167420	7.79545505	-1.09624094
H	5.75924238	8.09158370	-0.98810410
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H	5.62217383	8.15182841	1.56144225

H	3.87273925	7.86015067	1.49398908
H	4.91322449	6.78481593	2.45414310
C	6.50111819	5.85857900	0.38522040
H	6.62086783	5.26344828	1.29705736
H	6.72196555	5.22941424	-0.48384052
H	7.23380219	6.67205885	0.41082940
C	2.56224078	-4.14852844	-0.17889207
C	3.98077237	-4.29311924	-0.28401419
C	4.55885406	-5.54995172	-0.47569066
C	1.98934079	-2.89621672	0.00334334
C	4.80607191	-3.10895021	-0.18137444
C	4.22978889	-1.84213109	-0.00687242
C	2.77673643	-1.72410763	0.06556982
C	6.21802900	-3.27751433	-0.27189762
C	6.79387492	-4.52910901	-0.45923589
C	6.01036874	-5.68447334	-0.56905605
H	7.87224026	-4.57028482	-0.51810792
H	0.91281858	-2.80614652	0.10411298
C	3.71075756	-6.73003709	-0.58357667
C	1.68866334	-5.31159812	-0.28612826
C	5.09576312	-0.67064644	0.10181741
C	7.11493999	-2.13320186	-0.17249432
O	0.44190375	-5.26279898	-0.21842796
O	4.14864327	-7.90844815	-0.76076373
O	8.36056238	-2.22642755	-0.24391420
O	4.71070518	0.51135350	0.27175845
N	2.33758705	-6.54837213	-0.48651868
N	6.48159896	-0.89401109	0.01313365
C	7.34606344	0.30028004	0.12722638
H	8.37075539	-0.05605945	0.03920515
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H	7.17885507	0.78685799	1.09101585
C	1.49544697	-7.76219573	-0.60578465
H	1.75158516	-8.46652536	0.18845325
H	0.46381116	-7.42837326	-0.51932820
H	1.67712410	-8.24116729	-1.57002815
N	6.53650957	-6.91354148	-0.75551483
H	5.81971517	-7.66718037	-0.81667554
C	7.97110432	-7.18299853	-0.86351038
H	8.10753098	-8.25521112	-1.01359510
H	8.41161845	-6.64532217	-1.71202863
H	8.50017733	-6.88043879	0.04852132
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