

Supporting Information

Evolution from tunneling to hopping mediated triplet energy transfer from quantum dots to molecules

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1. Chemicals and Instrumentation.

Chemicals were purchased from Combi-Blocks, TCI America, Sigma-Aldrich and used as received. Dry and degassed tetrahydrofuran (THF), acetone, toluene were obtained from JC Meyer's solvent purification system. ACS grade acetone was purchased from Fisher and dried with MgSO_4 before use.

Proton NMR (^1H) spectra was recorded on Bruker Avance 500 MHz spectrometers; carbon NMR (^{13}C) spectra were recorded on a Bruker Avance NEO 400 MHz spectrometer. The ^1H and ^{13}C chemical shifts are reported in parts per million and the residual solvent peak was used as an internal standard at room temperature. High resolution mass spectrometry (HRMS) was recorded on an Agilent LCTOF using APCI/ESI ionization.

Linear absorption spectra were recorded on a Jasco-V670 UV-Vis absorption spectrophotometer. Ensemble fluorescence spectra were recorded on a HORIBA FluoroMax-3 fluorometer. Upconversion samples were prepared in the glove box with 1 cm air-free cuvettes. Upconversion fluorescence spectra were recorded at right angles to the excitation with an Ocean Optics Inc. Maya spectrometer. The 488 nm laser (OBIS) is focused to a spot with radius of 120.9 μm . The power density is 16.3 W/cm^2 . In front of the detector, a 488 nm StopLine single-notch filter (part number NF03-488E-25) is used to block the scattered laser light. The upconverted light was collected on the Maya Pro 2000 spectrometer through an Ocean Optics QP400-2-SR fiber. The upconversion quantum yields were calculated with a Rhodamine 6G reference excited with a 488 nm laser (OBIS).

Transient absorption spectroscopy is conducted on a home built ultrafast spectrometer with picosecond and nanosecond setup. The picosecond setup is based on a 1 kilohertz 150 femtosecond ultrafast laser (Coherent, Legend). The 2.2 W 800 nm output is split so that ~ 1.8 W is directed into an optical parametric amplifier (TOPAS, Spectra Physics), the 510 nm pump pulse is generated by the OPA. The remaining 0.4 W is split again, with half goes directly to

the BBO crystal for 400 nm generation and the other half is focused onto a sapphire plate for white light generation. The pump pulse is optically delayed and size-adjusted before arrives on the sample. The probe is focused on the sample and overlapped spatially with the pump pulse. The picosecond setup has a time window of 2 ns limited by the delay stage. The nanosecond setup shares the same pump pulse, but the whitelight probe is provided by a 2 kilohertz laser (Ultrafast systems). The delay is controlled electronically. The signal is collected and analyzed by Ultrafast systems software (Helios, Eos, Surface Xplorer). The sample is loaded under an Ar atmosphere glovebox (MBraun) into 1 mm pathlength quartz cell (Starna). The sample is stirred during experiment to avoid photodegradation.

The time-resolved photoluminescence (TR-PL) is based on an 80-megahertz oscillator (Tsunami, Spectra Physics). The output is pulse-picked to desired frequency (determined by the time window of interest). The output beam is frequency doubled by a BBO crystal to desired wavelength (430 nm in this study), the same sample in TAS study is excited by the pulse. The fluorescence is collected collinearly by a series of lens and filters to collimate the fluorescence while removing the excitation pulse. The fluorescence is focused into a monochromator before collected by a microplate photomultiplier tube. The TR-PL data is collected and processed by the TCSPC system (Becker&Hickel SPC 600).

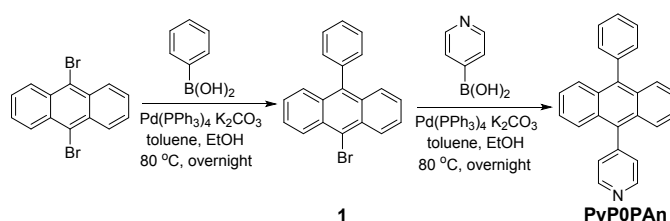
2. Synthesis of CdSe nanocrystals.

2.4 nm diameter wurtzite CdSe nanocrystals (NCs) were synthesized following the published method.¹ Specifically, trioctylphosphine oxide (TOPO) (3.0g), octadecylphosphonic acid (ODPA) (0.280g) and CdO (0.060g) were added to a 25mL three-neck round bottom flask. The trace amount of water in the mixture was removed by heating at 150°C for 1 hour. The flask was then refilled with argon and heated to above 350°C until CdO dissolved. Then 1.5 g trioctylphosphine (TOP) was injected into the flask. Heat the mixture to 370 °C, and the Se:TOP solution (0.058g Se + 0.360g TOP) was immediately injected. After 10s from injection, the heating mantle was quickly removed, and the reaction was cooled down with compressed air. CdSe NCs were washed in the glove box by methanol/toluene precipitation/redispersion three times. The CdSe NCs were dissolved in toluene and stored in dark in the glove box. The concentration and diameter of CdSe NCs were determined based on the literature.² The photoluminescence quantum yield of the CdSe NCs was measured to be 0.23 using Rhodamine 6G as the standard.

3. Synthesis of transmitter ligands

All transmitter ligands were recrystallized with (dichloromethane/*n*-hexanes) before use. All reactions were conducted under argon.

3. 1 Synthesis of PyP0PAn



9-bromo-10-phenylanthracene (**1**)

9,10-dibromoanthracene (2 g, 5.95 mmol), phenylboronic acid (725.5 mg, 5.95 mmol), tetrakis(triphenylphosphine)palladium(0) (687.6 mg, 0.595 mmol), K_2CO_3 (17.8 mL aqueous

solution, 2 M), toluene (35.6 mL) and ethanol (11.9 mL) were added to a 100 mL 2-necked round bottom flask equipped with a water condenser. The reaction was bubbled with argon for 15 min and stirred under reflux at 80 °C overnight. After cooling down to r.t., the product was extracted with dichloromethane 3 times from aqueous phase. The combined organic phase was then washed with brine and dried with MgSO₄. Solvents were removed on rotavap. The product was purified by column chromatography with the eluent of *n*-hexanes. Light yellow powder was obtained with the yield of 86.4%. NMR data is consistent with the published.³

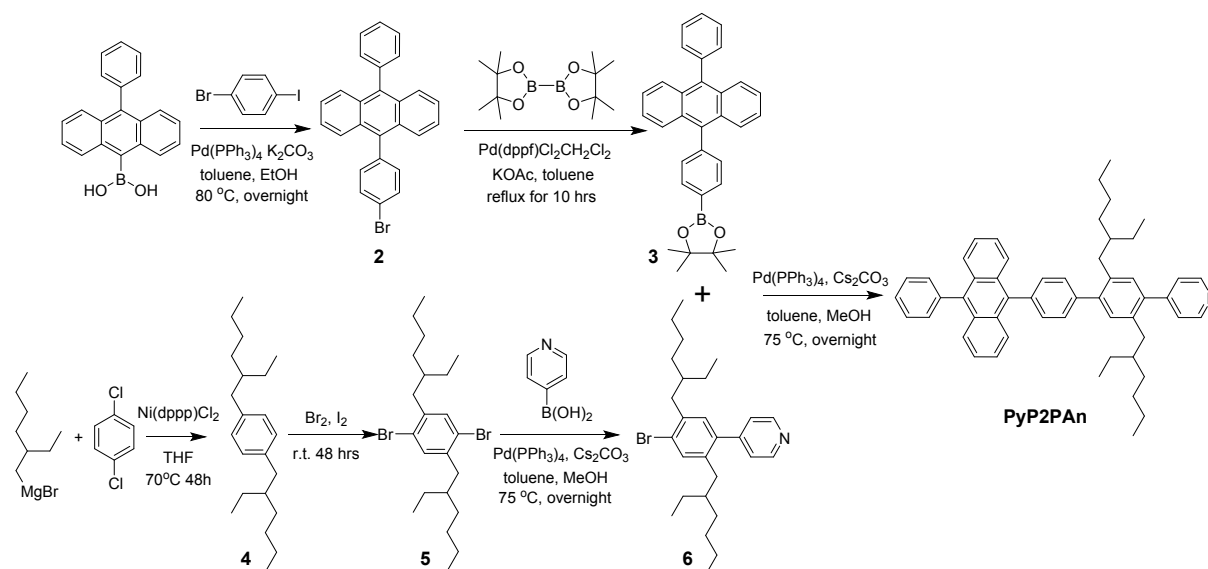
4-(10-phenylanthracen-9-yl)pyridine (**PyP0PAn**)

Compound **1** (1.98 g, 5.95 mmol), 4-pyridinylboronic acid (877.5 mg, 7.14 mmol), tetrakis(triphenylphosphine)palladium(0) (687.6 mg, 0.595 mmol), K₂CO₃ (17.8 mL aqueous solution, 2 M), toluene (35.6 mL) and ethanol (11.9 mL) were added to a 100 mL 2-necked round bottom flask equipped with a water condenser. The reaction was bubbled with argon for 15 min and stirred under reflux at 80 °C overnight. After cooling down to r.t., the product was extracted with dichloromethane 3 times from aqueous phase. The combined organic phase was then washed with brine and dried with MgSO₄. Solvents were removed on rotar-vap. Proton NMR revealed 40% conversion of the reaction. The crude product was loaded on silica gel column. *n*-hexanes was used to collect unreacted starting material **1**, and product was collected with 3:1 (v/v) *n*-hexanes: ethyl acetate. Light yellow powder was obtained with the yield of 24.0%. NMR data is consistent with the published.⁴

3. 2 Synthesis of **PyP1PAn**

The synthesis of **PyP1PAn** follows the published method.⁴

3. 3 Synthesis of PyP2PAn



9-(4-bromophenyl)-10-phenylanthracene (**2**)

10-phenyl-9-anthraceneboronic acid (100 mg, 0.335 mmol), 1-bromo-4-iodobenzene (94.9 mg, 0.335 mmol), Tetrakis(triphenylphosphine)palladium(0) (38.8 mg, 0.0335 mmol), K_2CO_3 (1.7 mL aqueous solution, 2 M), toluene (3.4 mL) and ethanol (1.7 mL) were mixed and bubbled with argon for 5 min and stirred under reflux at 80°C overnight. After cooling down to r.t., the product was extracted with dichloromethane 3 times from aqueous phase. The combined organic phase was then washed with brine and dried with MgSO_4 . Solvents were removed on rotar-vap. The product was purified by column chromatography with the eluent of *n*-hexanes. Light yellow powder was obtained with the yield of 70.0%. NMR data is consistent with the published.⁵

4,4,5,5-tetramethyl-2-(4-(10-phenylanthracen-9-yl)phenyl)-1,3,2-dioxaborolane (**3**)

Compound **2** (50 mg, 0.122 mmol), bis(pinacolato)diboron (37.8 mg, 0.149 mmol), $\text{Pd(dppf)Cl}_2\cdot\text{CH}_2\text{Cl}_2$ (3 mg, 0.00366 mmol), potassium acetate (35.9 mg, 0.366 mmol), toluene (1 mL) were added to the Schlenk tube and bubbled with argon for 5 min, then stirred under reflux at 115°C overnight. After cooling down to r.t., the product was extracted with

dichloromethane 3 times from aqueous phase. The combined organic phase was then washed with brine and dried with MgSO_4 . Solvents were removed on rotar-vap. The product was purified by column chromatography with the eluent of 9:1 (v/v) *n*-hexanes: ethyl acetate. White powder was obtained with the yield of 81.4%. NMR data is consistent with the published.⁶

1,4-bis(2-ethylhexyl)benzene (**4**)

Glassware was dried under vacuum with heat gun before use. 1,4-dichlorobenzene (500 mg, 3.40 mmol, dried under vacuum before use) and $\text{Ni}(\text{dppf})\text{Cl}_2$ (5.53 mg, 0.012 mmol) were dissolved in 13.3 mL anhydrous THF. 8.78 mL (2-Ethylhexyl) magnesium bromide solution (1 M in diethyl ether) was slowly added to the reaction and the mixture was stirred under reflux at 50 °C for 48 hours. After cooling down to the r.t., water and then 1 M HCl was added very slowly to quench the reaction. The product was extracted with dichloromethane 3 times from aqueous phase. The combined organic phase was then washed with brine and dried with MgSO_4 . Solvents were removed on rotar-vap. The product was purified by column chromatography with the eluent of *n*-hexanes. Colorless oil was obtained with the yield of 75.2%. NMR data is consistent with the published.⁷

1,4-dibromo-2,5-bis(2-ethylhexyl)benzene (**5**)

Compound **5** (2.21 g, 7.31 mmol), iodine crystal (18.5 mg, 0.073 mmol) were added to a 25 mL round bottom flask, and bromine (0.86 mL, 16.8 mmol) was added dropwise. The reaction was stirred at r.t. for 48 hours. 20% NaOH aqueous solution was then used to quench the reaction. The product was extracted with diethyl ether 3 times from aqueous phase. The combined organic phase was then washed with brine and dried with MgSO_4 . Solvents were removed on rotar-vap. The product was purified by column chromatography with the eluent of *n*-hexanes.

Light brown oil was obtained with the yield of 84.7%. NMR data is consistent with the published.⁸

4-(4-bromo-2,5-bis(2-ethylhexyl)phenyl)pyridine (**6**)

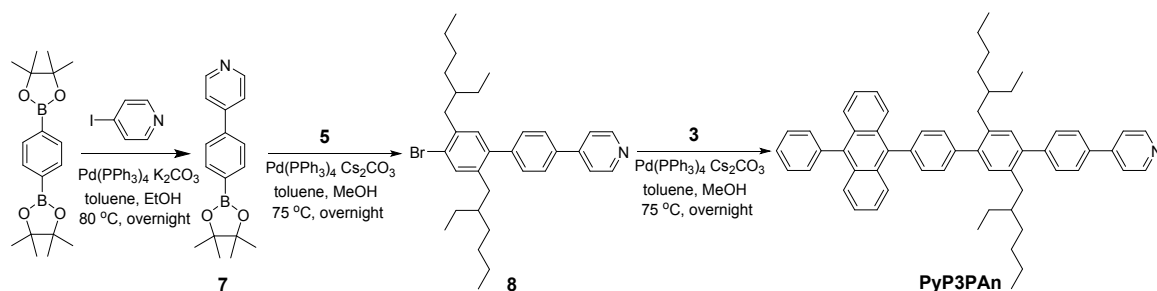
Compound **5** (2.8 g, 6.1 mmol), 4-pyridinylboronic acid (500 mg, 4.06 mmol), Tetrakis(triphenylphosphine)palladium(0) (470 mg, 0.406 mmol), Cs₂CO₃ (2.64 g, 8.12 mmol), anhydrous toluene (27 mL) and anhydrous methanol (27 mL) were added to a 100 mL 2-necked round bottom flask equipped with a water condenser. The reaction was bubbled with argon for 15 min and stirred under reflux at 76 °C overnight. After cooling down to r.t., the product was extracted with dichloromethane 3 times from aqueous phase. The combined organic phase was then washed with brine and dried with MgSO₄. Solvents were removed on rotar-vap. The product was purified by column chromatography with the eluent of 5:1 (v/v) of *n*-hexanes: ethyl acetate. Light brown gelly product was obtained with the yield of 78.3%. ¹H NMR (500 MHz, CDCl₃) δ 8.64 (d, J = 5.8 Hz, 2H), 7.43 (s, 1H), 7.20 (d, J = 5.8 Hz, 2H), 6.94 (s, 1H), 2.64 (d, J = 7.2 Hz, 2H), 2.46 (d, J = 7.2 Hz, 2H), 1.70 (m, 2H), 1.36 – 1.20 (m, 16H), 0.87 (m, 12H). ¹³C NMR (400 MHz, CDCl₃) δ 149.58, 138.89, 138.53, 134.91, 134.50, 132.25, 130.07, 127.97, 124.60, 40.54, 40.16, 39.40, 36.57, 32.49, 32.38, 28.82, 28.64, 25.75, 25.56, 23.18, 22.98, 14.22, 14.14, 10.92, 10.75. HRMS Calc.: 457.2347. Found ([M+H]⁺): 458.2421.

4-(2,5-bis(2-ethylhexyl)-4'-(10-phenylanthracen-9-yl)-[1,1'-biphenyl]-4-yl)pyridine
(**PyP2PAn**)

Compound **3** (34.8 mg, 0.076 mmol), compound **6** (35 mg, 0.076 mmol), tetrakis(triphenylphosphine)palladium(0) (8.8 mg, 0.076 mmol), Cs₂CO₃ (49.5 mg, 0.152 mmol), anhydrous toluene (1 mL) and anhydrous methanol (1 mL) were added to a Schlenk tube. The reaction was bubbled with argon for 5 min and stirred under reflux at 76 °C overnight.

After cooling down to r.t., the product was extracted with dichloromethane 3 times from aqueous phase. The combined organic phase was then washed with brine and dried with MgSO_4 . Solvents were removed on rotar-vap. The product was purified by column chromatography with the eluent of 5:1 (v/v) of *n*-hexanes: ethyl acetate. Light yellow powder was obtained with the yield of 55.8%. ^1H NMR (500 MHz, CDCl_3) δ 8.70 (d, $J = 4.9$ Hz, 2H), 7.85 – 7.79 (m, 2H), 7.75 – 7.70 (m, 2H), 7.66 – 7.60 (m, 2H), 7.60 – 7.53 (m, 5H), 7.53 – 7.49 (m, 2H), 7.36 (m, 6H), 7.32 (s, 1H), 7.11 (s, 1H), 2.79 (m, 1H), 2.71 (m, 1H), 2.63 (d, $J = 7.2$ Hz, 2H), 1.78 – 1.68 (m, 2H), 1.36 – 1.03 (m, 28H). ^{13}C NMR (400 MHz, CDCl_3) δ 142.13, 141.14, 139.20, 138.36, 137.69, 137.34, 137.30, 137.03, 136.40, 132.45, 131.80, 131.47, 131.22, 130.09, 129.55, 128.57, 127.64, 127.19, 127.09, 125.16, 124.94, 40.67, 40.50, 37.31, 36.93, 32.57, 32.47, 29.85, 28.73, 25.77, 25.02, 23.16, 23.06, 14.18, 10.87. Calc. 707.4507. Found ($[\text{M}+\text{H}]^+$): 708.4581.

3. 4 Synthesis of PyP3PAn



4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyridine (**7**)

1,4-Benzenediboronic acid bis(pinacol) ester (2.254g, 6.83 mmol), 4-iodopyridine (1 g, 4.88 mmol), tetrakis(triphenylphosphine) palladium(0) (563.9 mg, 0.488 mmol), K_2CO_3 (12.2 mL aqueous solution, 2 M), toluene (9.8 mL) and ethanol (39 mL) were added to a 100 mL 2-necked round bottom flask equipped with a water condenser. The reaction was bubbled with argon for 15 min and stirred under reflux at 80°C overnight. After cooling down to r.t., the product was extracted with dichloromethane 3 times from aqueous phase. The combined

organic phase was then washed with brine and dried with MgSO₄. Solvents were removed on rotar-vap. The product was purified by column chromatography with the eluent of 4:1 (v/v) of *n*-hexanes: ethyl acetate. Light yellow solid was obtained with the yield of 70.6%. ¹H NMR (500 MHz, CDCl₃) δ 8.67 (d, *J* = 5.9 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 6.1 Hz, 2H), 1.37 (s, 12H). ¹³C NMR (400 MHz, CDCl₃) δ 150.34, 148.37, 140.79, 135.64, 126.40, 121.87, 84.18, 75.16, 25.01. HRMS. Calc.: 280.1627. Found ([M+H]⁺): 281.1679.

4-(4'-bromo-2',5'-bis(2-ethylhexyl)-[1,1'-biphenyl]-4-yl)pyridine (**8**)

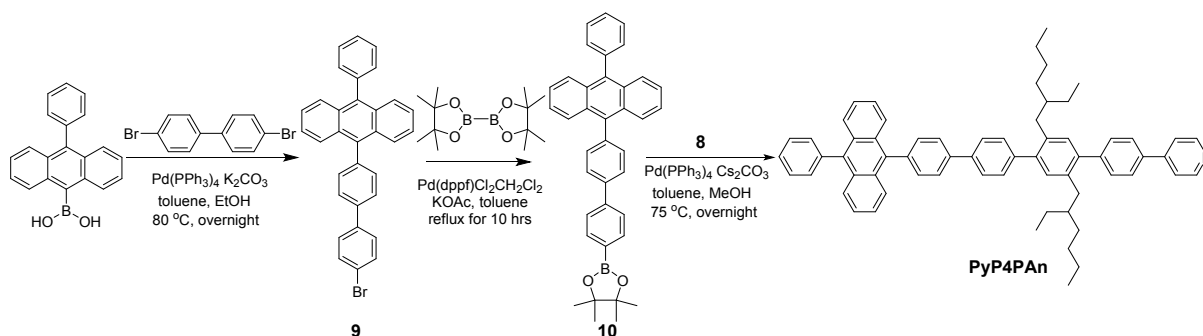
Compound **5** (140.4 mg, 0.305 mmol), compound **7** (57.1 mg, 0.203 mmol), tetrakis(triphenylphosphine)palladium(0) (23.5 mg, 0.0203 mmol), Cs₂CO₃ (132.3 mg, 0.406 mmol), anhydrous toluene (1.35 mL) and anhydrous methanol (1.35 mL) were added to a Schlenk tube. The reaction was bubbled with argon for 5 min and stirred under reflux at 76 °C overnight. After cooling down to r.t., the product was extracted with dichloromethane 3 times from aqueous phase. The combined organic phase was then washed with brine and dried with MgSO₄. Solvents were removed on rotar-vap. The product was purified by column chromatography with the eluent of 3:1 (v/v) of *n*-hexanes: ethyl acetate. Light brown jelly product was obtained with the yield of 50.0%. ¹H NMR (500 MHz, CDCl₃) δ 8.68 (d, *J* = 6.1 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 6.1 Hz, 2H), 7.43 (s, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.01 (s, 1H), 2.65 (d, *J* = 7.2 Hz, 2H), 2.60 – 2.43 (m, 2H), 1.73 (m, 2H), 1.39 – 1.20 (m, 12H), 1.19 – 0.91 (m, 16H). ¹³C NMR (400 MHz, CDCl₃) δ 150.28, 147.97, 142.31, 140.31, 138.81, 138.36, 136.61, 134.13, 132.69, 130.12, 126.70, 123.88, 121.52, 41.05, 40.31, 40.06, 39.71, 39.31, 36.85, 36.59, 32.39, 28.86, 28.72, 28.55, 25.63, 25.49, 23.06, 10.81, 10.69. HRMS. Calc. 533.2666 Found ([M+H]⁺): 534.2739.

4-(2',5'-bis(2-ethylhexyl)-4''-(10-phenylanthracen-9-yl)-[1,1':4,1''-terphenyl]-4-yl)pyridine

(PyP3PAn)

Compound **8** (54 mg, 0.101 mmol), compound **3** (46 mg, 0.101 mmol), tetrakis(triphenylphosphine)palladium(0) (11.7 mg, 0.0101 mmol), Cs₂CO₃ (65.8 mg, 0.202 mmol), anhydrous toluene (1 mL) and anhydrous methanol (1 mL) were added to a Schlenk tube. The reaction was bubbled with argon for 5 min and stirred under reflux at 76 °C overnight. After cooling down to r.t., the product was extracted with dichloromethane 3 times from aqueous phase. The combined organic phase was then washed with brine and dried with MgSO₄. Solvents were removed on rotar-vap. The product was purified by column chromatography with the eluent of 4:1 (v/v) of *n*-hexanes: ethyl acetate. Light yellow solid was obtained with the yield of 65.7%. ¹H NMR (500 MHz, CDCl₃) δ 8.70 (d, *J* = 6.1 Hz, 2H), 7.85 – 7.80 (m, 2H), 7.78 – 7.69 (m, 4H), 7.66 – 7.47 (m, 13H), 7.42 – 7.34 (m, 4H), 7.31 (s, 1H), 7.17 (s, 1H), 2.79 (m, 1H), 2.75 – 2.60 (m, 3H), 1.42 (m, 2H), 1.35 – 0.99 (m, 18H), 0.86 – 0.74 (m, 10H). ¹³C NMR (400 MHz, CDCl₃) δ 150.19, 148.52, 143.57, 141.45, 141.34, 140.33, 139.23, 137.50, 137.30, 137.14, 136.95, 136.75, 136.36, 132.29, 131.48, 131.16, 130.54, 130.12, 130.07, 129.64, 128.57, 127.64, 127.16, 126.80, 125.14, 121.75, 40.58, 40.56, 37.37, 37.09, 32.64, 28.80, 25.89, 25.80, 23.19, 23.07, 14.23, 14.22, 10.97, 10.89. HRMS Calc. 783.4824. Found ([M+H]⁺): 784.4898.

3. 5 Synthesis of PyP4PAn



9-(4'-bromo-[1,1'-biphenyl]-4-yl)-10-phenylanthracene (**9**)

10-phenyl-9-anthraceneboronic acid (1 g, 3.36 mmol), 4,4'-Dibromobiphenyl (3.15 g, 10.1 mmol), tetrakis(triphenylphosphine)palladium(0) (388 mg, 0.336 mmol), K₂CO₃ (10 mL aqueous solution, 2 M), toluene (21 mL) and ethanol (6.8 mL) were added to a 100 mL 3-necked round bottom flask and bubbled with argon for 15 min, then stirred under reflux at 80 °C overnight. After cooling down to r.t., the product was extracted with dichloromethane 3 times from aqueous phase. The combined organic phase was then washed with brine. As the product is not very soluble in dichloromethane, no MgSO₄ drying and the subsequent filtration were performed. Dichloromethane was removed on rotar-vap. The product was purified by column chromatography with the eluent of dichloromethane. White solid was obtained with the yield of 89.3%. NMR data is consistent with the published.⁴

4,4,5,5-tetramethyl-2-(4'-(10-phenylanthracen-9-yl)-[1,1'-biphenyl]-4-yl)-1,3,2-dioxaborolane (**10**)

Compound **9** (815 mg, 1.68 mmol), bis(pinacolato)diboron (520 mg, 2.05 mmol), Pd(dppf)Cl₂·CH₂Cl₂ (41 mg, 0.05 mmol), potassium acetate (495 mg, 5.04 mmol), toluene (12 mL) were added to the 25 mL 2-necked round bottom flask and bubbled with argon for 15 min, then stirred under reflux at 115 °C overnight. After cooling down to r.t., the product was extracted with dichloromethane 3 times from aqueous phase. The combined organic phase was then washed with brine and dried with MgSO₄. Solvents were removed on rotar-vap. The product was purified by column chromatography with the eluent of 9:1 (v/v) of *n*-hexanes: ethyl acetate. White powder was obtained with the yield of 86.6%. NMR data is consistent with the published.⁴

4-(2',5'-bis(2-ethylhexyl)-4'''-(10-phenylanthracen-9-yl)-[1,1':4',1'':4'',1'''-quaterphenyl]-4-yl)pyridine (**PyP4PAn**)

Compound **8** (300 mg, 0.561 mmol), compound **10** (299 mg, 0.561 mmol), tetrakis(triphenylphosphine)palladium(0) (65 mg, 0.0561 mmol), Cs₂CO₃ (366 mg, 1.12 mmol), anhydrous toluene (3.7 mL) and anhydrous methanol (3.7 mL) were added to a Schlenk tube. The reaction was bubbled with argon for 10 min and stirred under reflux at 76 °C overnight. After cooling down to r.t., the product was extracted with dichloromethane 3 times from aqueous phase. The combined organic phase was then washed with brine and dried with MgSO₄. Solvents were removed on rotar-vap. The product was purified by column chromatography with the eluent of 4:1 (v/v) of *n*-hexanes: ethyl acetate. Light yellow solid was obtained with the yield of 22.6%. NMR data is consistent with the published.⁴

4.

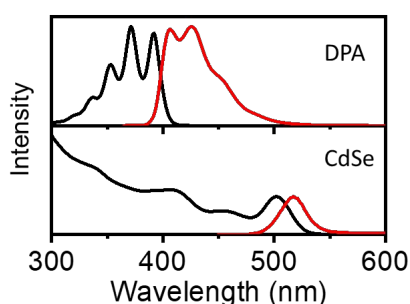


Figure S1. Absorption (black) and fluorescence (red) spectra of emitter 9,10-diphenylanthracene (DPA) and CdSe nanocrystals. The spectra were obtained in hexane at room temperature.

5. Calculation of upconversion quantum yield

Upconversion quantum yield

$$\Phi_{UC} = 2 \times \Phi_{ref} \times \frac{(\text{photons absorbed by reference})}{(\text{photons absorbed by UC sample})} \times \frac{PL \text{ signal}(UC \text{ sample})}{PL \text{ signal}(\text{reference})}$$

where Φ_{ref} is the fluorescence QY of rhodamine 6G.⁹ The pre-factor of 2 allows 100% upconversion QY to be defined as the emission of 50 upconverted photons per 100 absorbed photons.

$$photon\ absorbed = 1 - 10^{-abs}$$

where *abs* is the absorbance of the sample at excitation wavelength (488 nm).

6. Sample preparation for upconversion and transient absorption measurements.

A ligand exchange solution was prepared in a N₂ glovebox by mixing CdSe NC stock solution (in toluene) and the solution of transmitter ligand THF solution. With a total volume of 200 μ L, the concentration of CdSe NCs is 64.9 μ M, and the concentration of transmitter ligand is designated in Figure S2. The mixture was stirred overnight. 1 mL acetone was then added to the ligand solution, followed by the centrifugation at 7830 rpm for 10 min. The supernatant was discarded. For the photon upconversion measurement, the CdSe pellet was redispersed in 2.15 mM 9,10-diphenylanthracene in *n*-hexanes and transferred to 1 cm air-tight quartz cuvette. For transient absorption measurements, the CdSe pellet was redispersed in *n*-hexanes. This solution was then transferred to 1 mm air-tight quartz cuvette.

A different procedure was followed for the preparation of the transient absorption sample in Figure 4: 40 μ L CdSe NC stock solution was added to the 0.6 mL THF solution of PyP4PAn. The mixture contains 4.06 μ M CdSe NCs and 0.182 M PyP4PAn, which was stirred overnight and transferred to 1 mm air-tight quartz cuvette for transient absorption measurement.

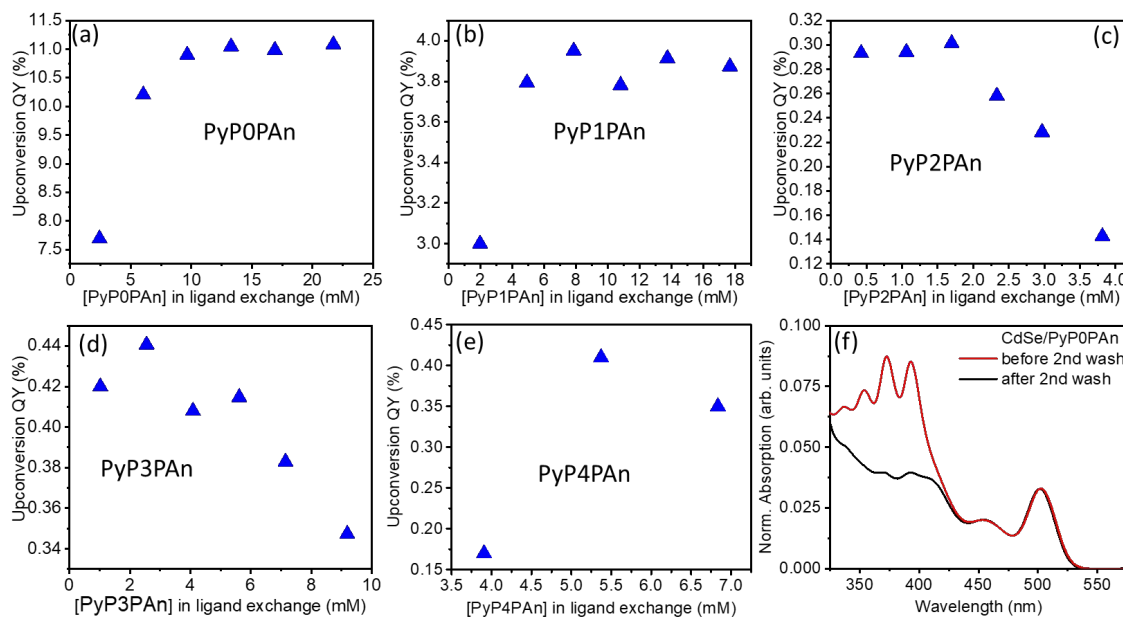


Figure S2. (a)-(e) Upconversion quantum yield versus the concentration of transmitter ligands during ligand exchange for **PyP0PAn** to **PyP4PAn**, respectively. (f) Absorption spectra of CdSe/PyP0PAn complex with optimal loading before (red) and after (black) a second wash following section 5.

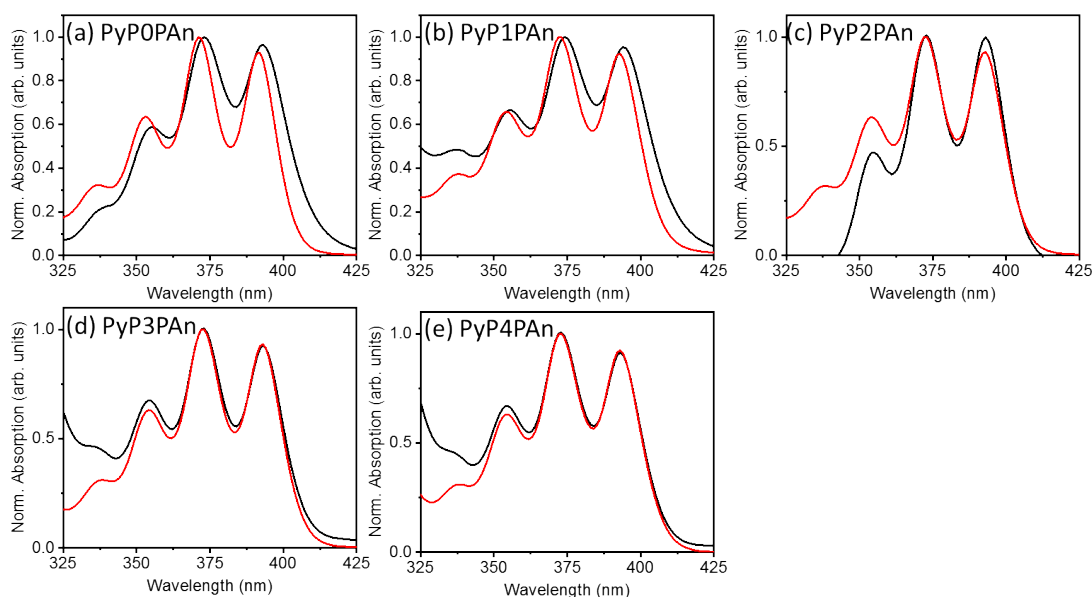


Figure S3. UV-Vis absorption spectra of bound (black) and free (red) transmitter ligands PyP0PAn-PyP4PAn. The spectra of transmitters bound on CdSe NCs are obtained by subtracting the spectra of CdSe NC from that of CdSe/transmitter complexes after normalization at first excitonic peak. The spectra of free and bound transmitter ligands are normalized at λ_{max} .

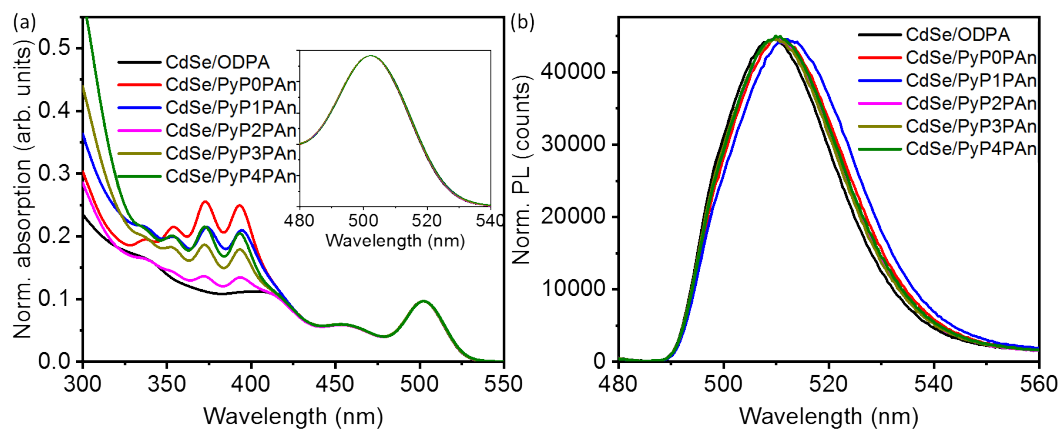


Figure S4. (a) UV-Vis absorption spectra of CdSe NCs capped with ODPA ligand and PyP0PAn-PyP4PAn transmitter ligands with normalization at CdSe first excitonic peak. Inset: zoom-in at CdSe first excitonic peak. (b) Photoluminescence of CdSe NC from samples in (a) after normalization. Samples are used for transient absorption and photoluminescence spectroscopy. Samples are prepared in hexane and measured at room temperature.

7. Transient absorption spectra of transmitters

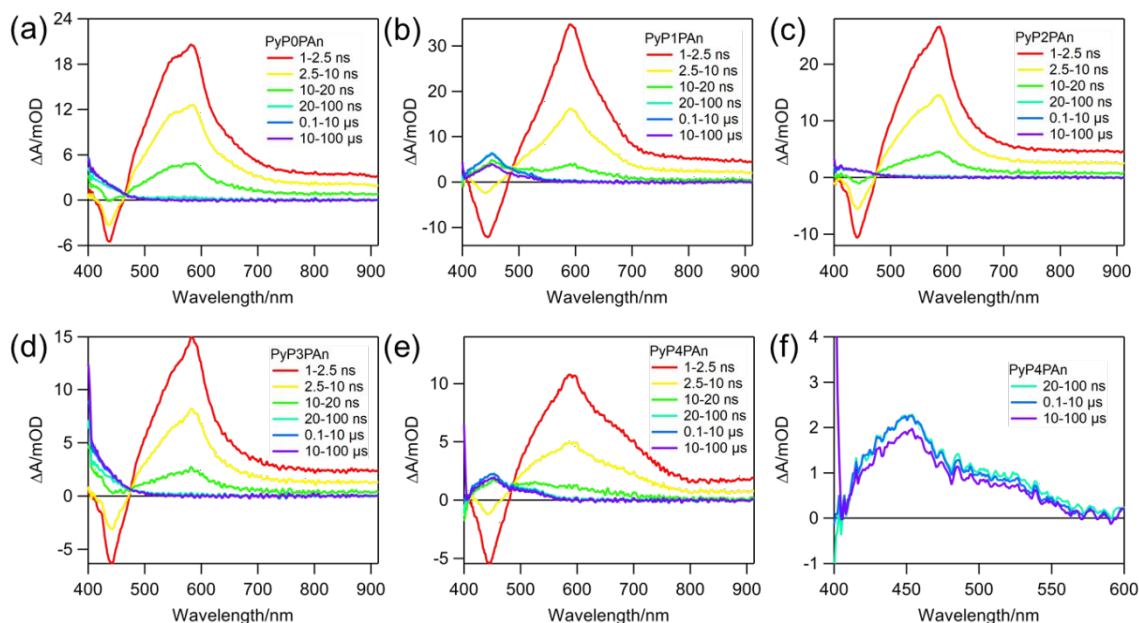


Figure S5. Nanosecond transient absorption spectra of pristine PyP0PAn to PyP4PAn with 400 nm excitation in hexane. The negative peak at ~440 nm is the ground state bleach and the positive peak at ~600 nm is the excited state absorption of singlet state. The triplet ESA is centered at ~440 nm at later times. (f) The triplet state ESA is magnified for PyP4PAn.

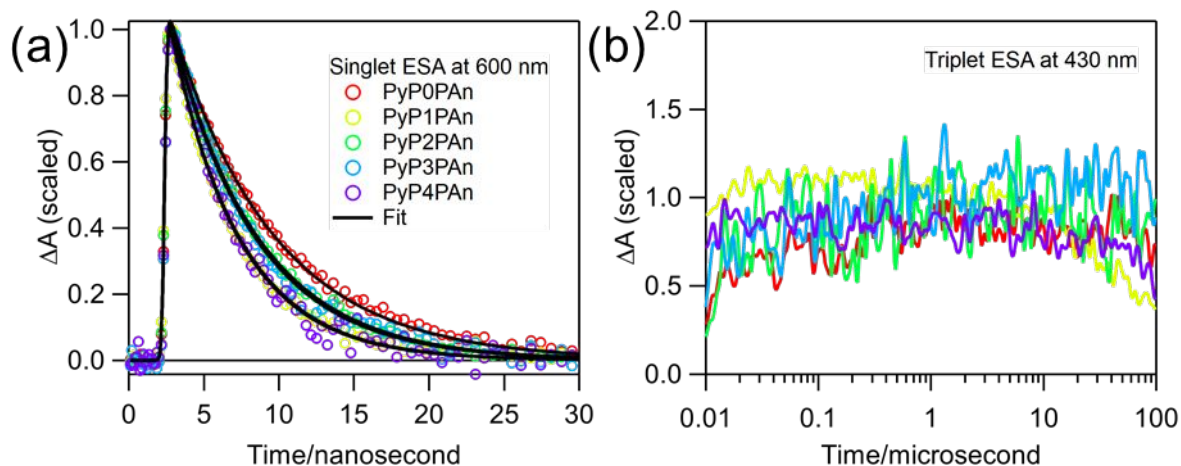


Figure S6. (a) Singlet kinetics probed at 600 nm of PyP0PAn to PyP4PAn in Figure S5 and (b) triplet lifetime probed at 430 nm with the same legend from PyP0PAn to PyP4PAn. All transmitters have triplet lifetime over 100 μ s. The singlet kinetics is fitted with a single exponential decay by $e^{-t/\tau}$. The fitting result is shown in Table S1.

Table S1. Singlet lifetime from fitting.

Molecule	Singlet/ns
PyP0PAn	6.85±0.06
PyP1PAn	4.54±0.04
PyP2PAn	5.76±0.05
PyP3PAn	5.59±0.05
PyP4PAn	4.62±0.04

8. Time-resolved spectroscopy of CdSe-transmitter complexes

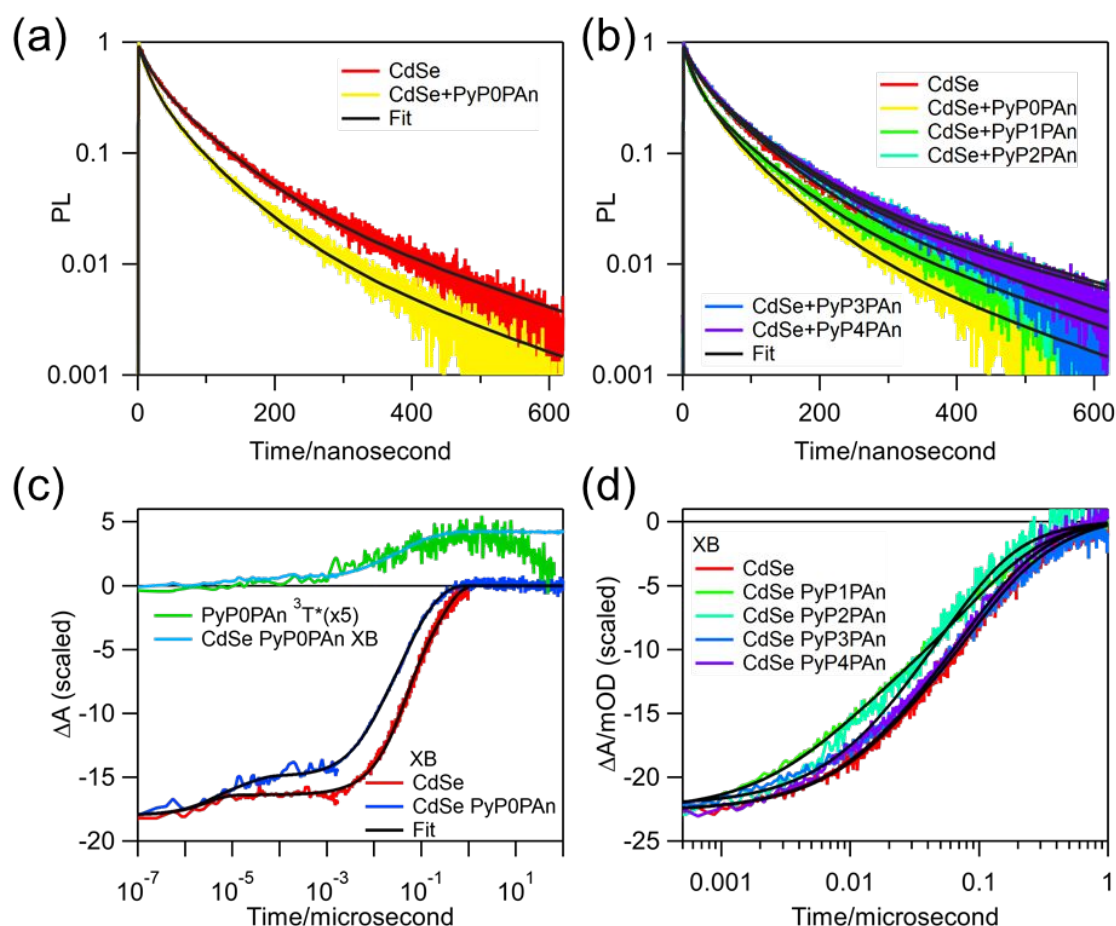


Figure S7. (a)-(b) CdSe TR-PL kinetics with no transmitter and PyP0PAn-PyP4PAn. (c)-(d) CdSe exciton bleach kinetics probed at 500 nm with no transmitter and PyP0PAn-PyP4PAn in nanosecond time scale. Notice in (b) the CdSe-PyP3PAn, CdSe-PyP4PAn exciton bleach kinetics are very similar to CdSe. Same for (d) CdSe-PyP3PAn and CdSe-PyP4PAn shows very similar PL decay with CdSe. This suggests the TET rate is very slow, and the TET efficiency is small. The fitting is described below.

9. Fitting to the data of time-resolved spectroscopy

The CdSe QD exciton kinetics by itself could be described by:

$$QD(t) = QD(0) \sum_{i=1}^3 a_i e^{-k_i t}$$

Here, k_i is the recombination rate of QD. Multiple k are due to the inhomogeneous distribution of exciton lifetime and decay pathway of QD assembly.

The same exciton kinetics when a transmitter is attached is:

$$QD(t) = QD(0) \sum_{i=1}^3 a_i e^{-(k_i + k_{TET})t}$$

However, sometimes a single k_{TET} does not provide a good fit to the experimental data.

Additional k_{TET} is added when this happens:

$$QD(t) = QD(0) \sum_{j=1}^2 \sum_{i=1}^3 b_j a_i e^{-(k_i + k_{TETj})t}$$

Multiple TET rates might arise from different binding geometry of transmitter on QD surface.

The TA and TR-PL kinetics can both be fitted to this equation and the results of these fitting are listed in Table S2. Additional electron trapping process could be described by an extra exponential term with rate constant k_{ET} with a weighting factor c .

The efficiency for each k_{TET} is calculated as:

$$\eta_j = b_j \left(\sum_{i=1}^3 \frac{a_i k_{TETj}}{k_{TETj} + k_i} \right) / \sum_{i=1}^3 a_i$$

And the averaged rate of TET is calculated as:

$$k_{TET} = \sum_{j=1}^2 b_j k_{TETj}$$

Finally, the total TET efficiency is:

$$\eta = \sum_{j=1}^2 \eta_j$$

Table S2. Fitting parameter of TET rate and efficiency by TAS and TR-PL.

parameter	CdSe		CdSe-PyP0PAn	
	TA	PL	TA	PL
$k_{TET}/\mu s^{-1}$	-	-	31.5	54.0
η_1 %			29.2	19.0
η_2 %			32.4	11.0
η %	-	-	61.6	30.1
a_1	0.114	0.412	-	-
a_2	0.538	0.519	-	-
a_3	0.920	0.069	-	-
$k_1/\mu s^{-1}$	3.26×10^5	61.6	-	-
$k_2/\mu s^{-1}$	25.9	15.0	-	-
$k_3/\mu s^{-1}$	3.64	4.67	-	-
b_1	-	-	0.240	0.314
b_2	-	-	0.760	0.686
$k_{TET1}/\mu s^{-1}$	-	-	122	40.7
$k_{TET2}/\mu s^{-1}$	-	-	2.96	0.383
$k_{ET}/\mu s^{-1}$	-	-	3.9×10^4	-
c	-	-	0.089	-

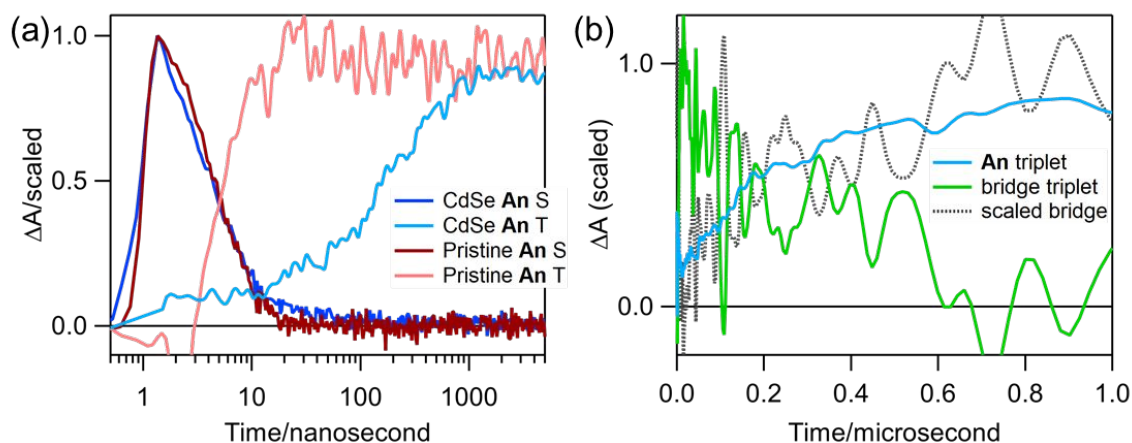


Figure S8. (a) The PyP4PAn singlet probed at 600 nm and triplet kinetics probed at 443 nm measured in pristine PyP4PAn (red, 440 nm excitation) and in the CdSe-PyP4PAn complex (blue, 510 nm excitation). In pristine PyP4PAn the triplet formation follows the singlet decay, because the triplet is formed via intersystem crossing from the singlet state. In CdSe PyP4PAn complexes, the decay of the singlet state (generated by two photon absorption) decay in the same way as pristine PyP4PAn, which is responsible for $\sim 5\%$ of the triplet population; 95% of the triplet population is formed on a much slower time scale through bridge mediated triplet energy transfer from the QD. (b) The growth of PyP4PAn triplet state (blue, probed at 443 nm) agrees well with the decay of bridge triplet (green, probed at 813 nm), indicating that the triplet formation is by hopping through the bridge triplet from the QD. Also shown is an inverted curve of the bridge triplet decay (grey) to allow better comparison with the anthracene triplet formation.

10. References

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