A Highly Efficient Light-Harvesting System with sequential energy transfer Based on Multicharged Supramolecular Assembly

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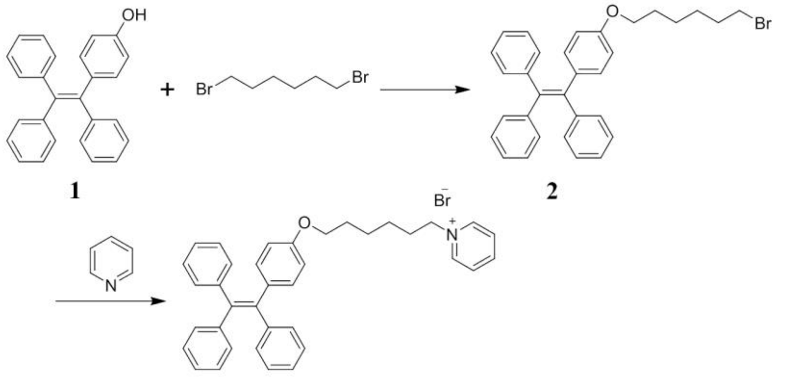
Experimental section

1. Instrumentation and methods

All the reagents and solvents were commercially available and used as received unless otherwise specified purification. All aqueous solutions were prepared in distilled water. Sulforhodamine 101(SR101), Eosin Y(EY), Nile red (NiR) and sulfonated aluminum phthalocyanine ($AlPcS_4$) were purchased from Sigma-Aldrich. NMR spectra were recorded on a Bruker AV400 instrument. UV/vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer in a quartz cell (light path 10 mm) at 25 °C. Steady-state fluorescence emission spectra were recorded in a conventional quartz cell (10 × 10 × 45 mm) at 25 °C on a Varian Cary Eclipse equipped with a Varin Cary single-cell peltier accessory to control temperature. The fluorescence lifetimes were measured by time-correlated single photon counting on a FLS920 instrument (Edinburg Instruments Ltd., Livingstone, UK). TEM images were acquired by a high-resolution transmission electron microscope (Philips Tecnai G2 20 S-TWIN microscope) operating at an accelerating voltage of 200 keV. The samples were prepared by placing a drop of solution onto a carbon-coated copper grid and air-dried. The zeta potential was recorded on NanoBrook 173Plus (Brookhaven company) at 25 °C. The sample solutions for dynamic light scattering measurements (DLS) were examined on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (Turbo Corr.) at 636 nm at a scattering angle of 90°.

2. Synthesis and characterization of Py-TPE



Scheme S1. Synthetic routes to the pyridinium modified tetraphenylethene derivative (**Py-TPE**)

The compound of **2**[1] (200 mg, 0.4mmol) and pyridine (500mg, 6mmol) in acetone (10 mL) was stirred for 24 h at 80 °C. After cooling to room temperature, lots of white solid powder was precipitated. Then the precipitate was filtered and washed with acetone, then dried under vaccum for 24 h to give **Py-TPE** as white solid (210 mg, 91% yield). ^{1}H NMR (400 MHz, DMSO) δ: 9.11 (d, J = 5.7 Hz, 2H), 8.60 (t, J = 7.8 Hz, 1H), 8.16 (t, J = 7.0 Hz, 2H), 7.18 – 7.06 (m, 9H), 6.96 (dd, J = 15.5, 7.4 Hz, 6H), 6.84 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 8.7 Hz, 2H), 4.61 (t, J = 7.4 Hz, 2H), 3.85 (t, J = 6.2 Hz, 2H), 1.98–1.88 (m, 2H), 1.65 (dd, J = 13.7, 6.5 Hz, 2H), 1.45–1.27 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ: 157.11, 145.44, 144.73, 143.50, 143.43, 143.39, 140.17, 139.62, 135.22, 131.87, 130.63, 130.62, 128.05, 127.84, 127.73, 126.43, 126.35, 126.32, 113.63, 67.00, 60.66, 30.58, 28.35, 25.09, 24.91. HR-MS (MALDI-TOF): m/z calcd for $C_{37}H_{36}NO^+$: 510.2796 [M]$^+$, found: 510.2795.

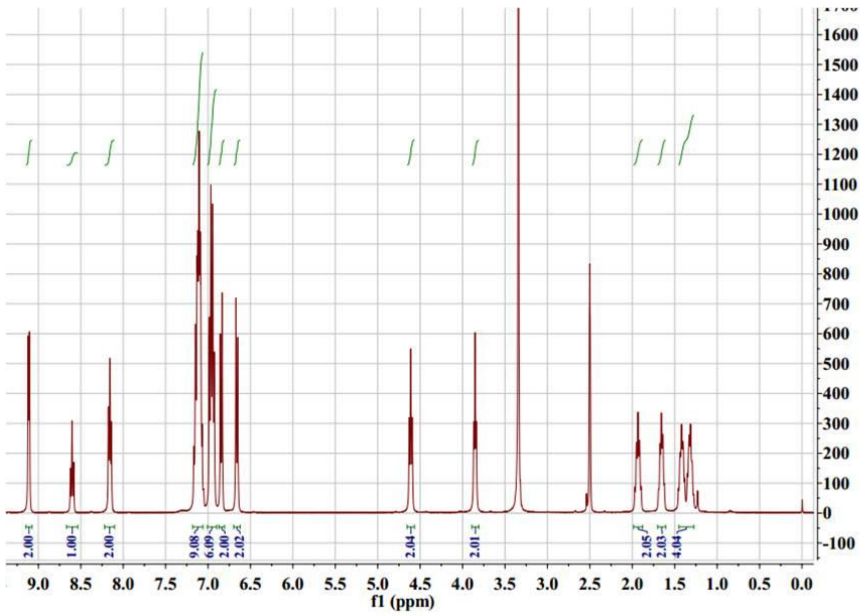


Fig S1. ^{1}H NMR (400 MHz) spectrum of **Py-TPE** in DMSO-d_6 at 25°C.

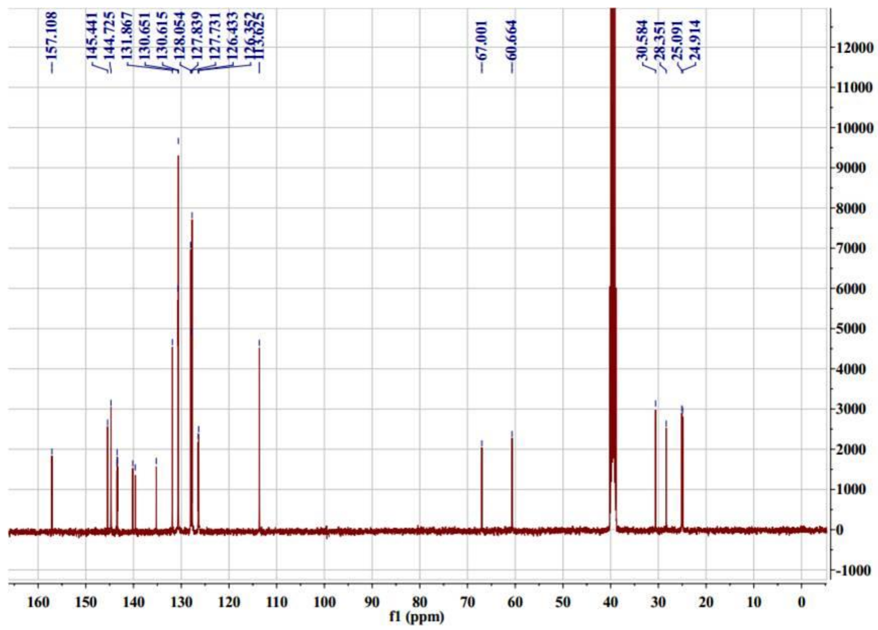


Fig S2. ^{13}C NMR (400 MHz) spectrum of **Py-TPE** in DMSO-d_6 at 25°C.

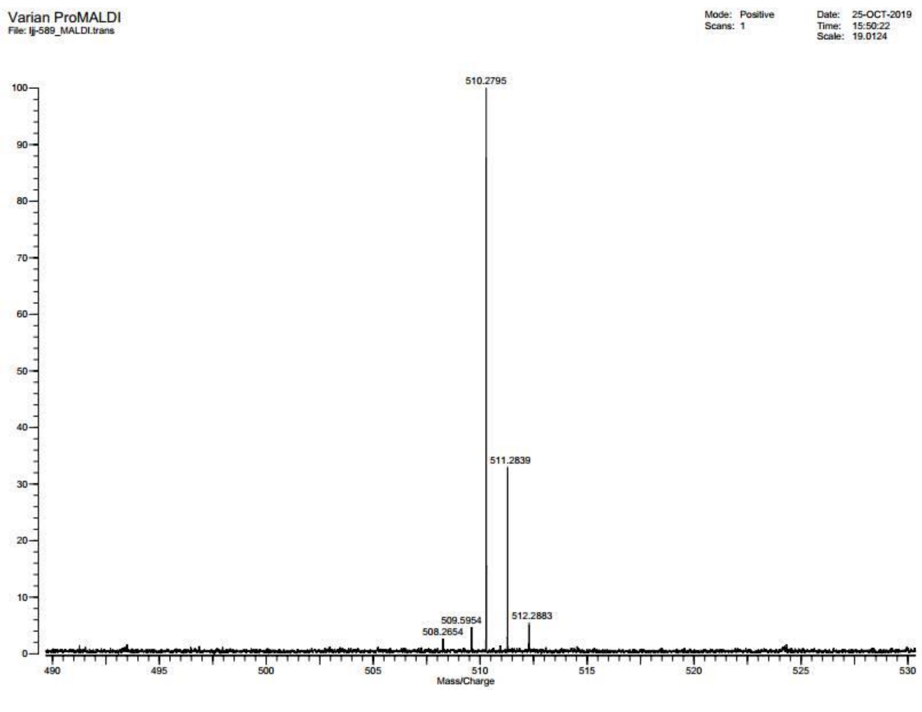


Fig S3. MALDI-MS spectrum of **Py-TPE**.

3. Characterization of Py-TPE/WP5

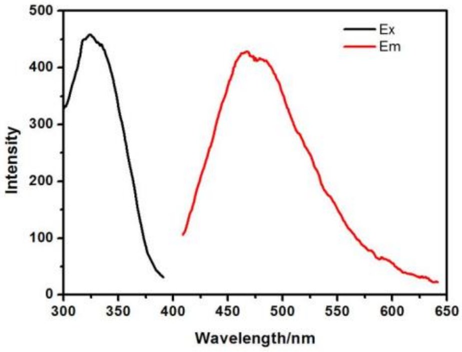


Fig S4. Excitation and emission spectra of **Py-TPE/WP5.**

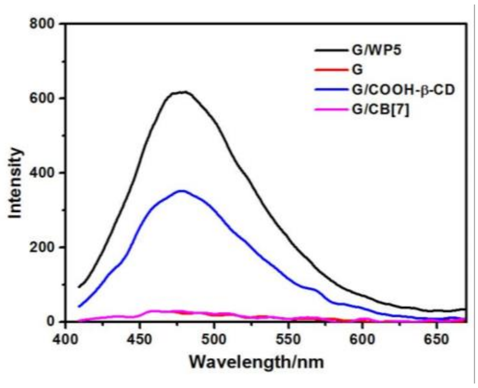


Fig S5. Fluorescence spectra of **Py-TPE** with the addition of **WP5**, **COOH-β-CD**, and **CB[7]** in aqueous solution (**[WP5]** = **[COOH-β-CD]** = **[CB[7]]** = 2 μM, **[Py-TPE]**=20 μM).

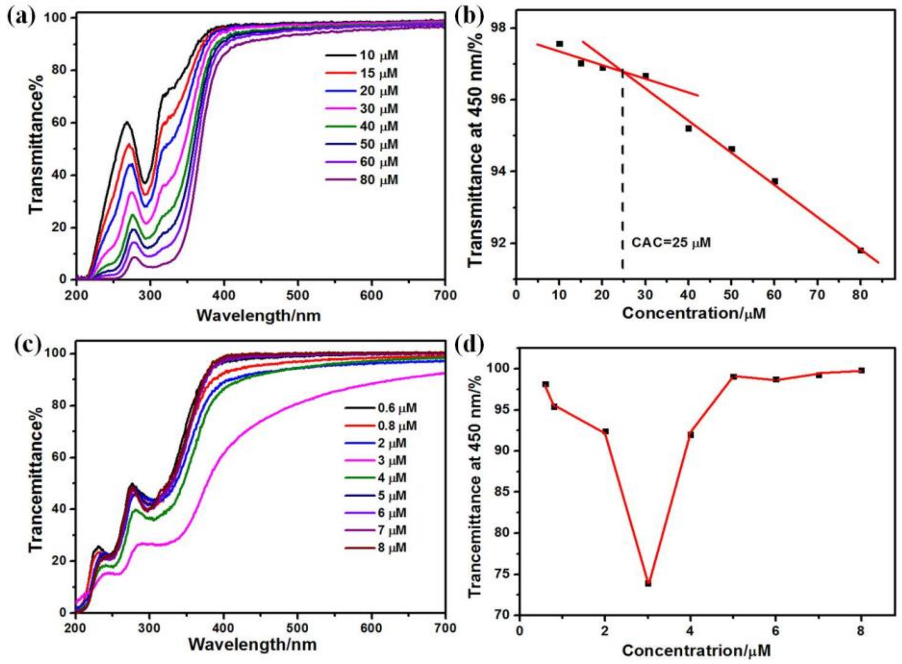


Fig S6. (a) Optical transmittance of **WP5** (20 μM) with **Py-TPE** at different concentrations in water at 25 °C. (b) Dependence of the optical transmittance at 450 nm on the **Py-TPE** concentration in the prescence of **WP5** (20 μM) in water at 25 °C. (c) Optical transmittance of **Py-TPE** (30 μM) with **WP5** at different concentrations in water at 25 °C. (d) Dependence of the optical transmittance at 450 nm on the **WP5** concentration with a fixed **Py-TPE** concentration (30 μM) in water at 25 °C.

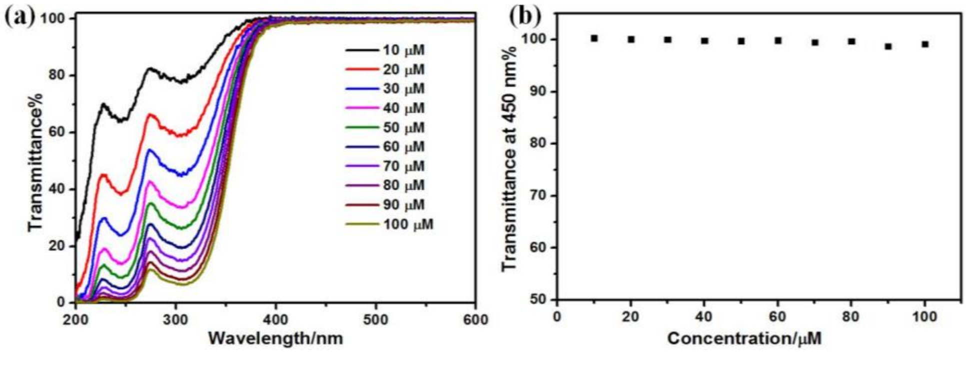


Fig S7. (a) Optical transmittance of **Py-TPE** at experiment concentration in water at 25 °C.(b) Dependence of the optical transmittance at 450 nm of **Py-TPE** in water at 25 °C.

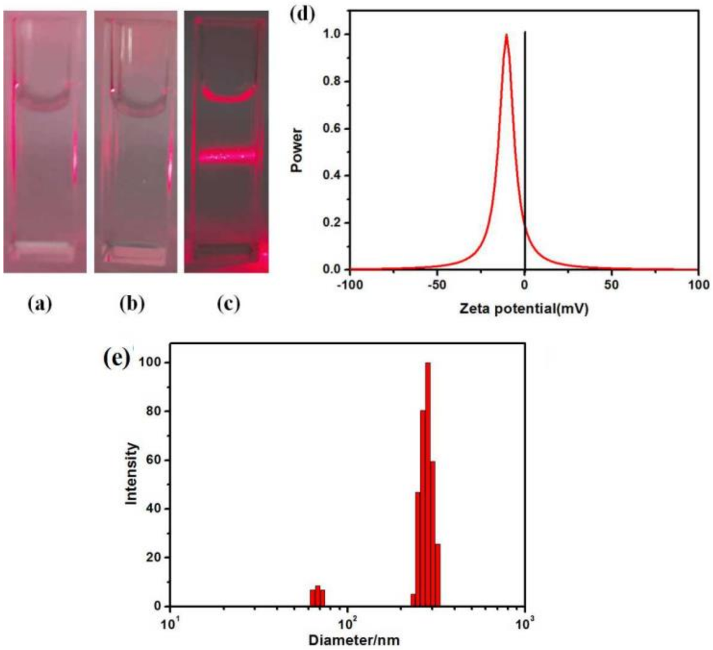


Fig S8. The Tyndall effect of (a) **WP5**, (b) **Py-TPE**, and (c) **Py-TPE/WP5** at the same concentration. (d) Zeta potential and (e) DLS of **Py-TPE/WP5.**

4. Construction and characterization of one-step energy transfer in aqueous solution

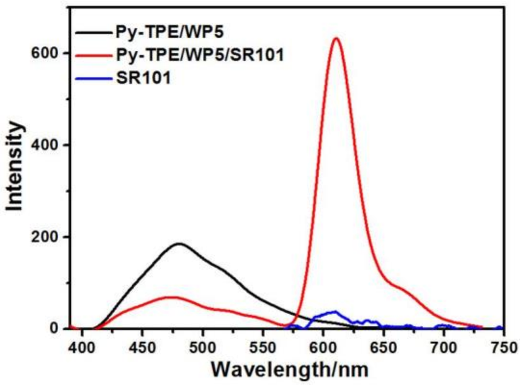


Fig S9. Fluorescence spectra of **Py-TPE/WP5**, **Py-TPE/WP5/SR101** and **SR101** in water (λ_{ex}=350 nm) (**Py-TPE** =20 μM, **WP5**=2 μM, **SR101**= 0.13 μM).

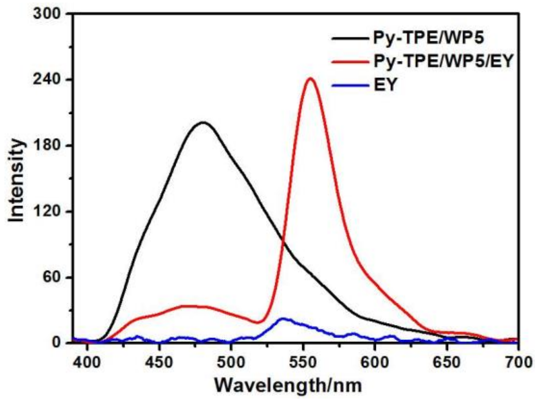


Fig S10. Fluorescence spectra of **Py-TPE/WP5**, **Py-TPE/WP5/EY** and **EY** in water (λ_{ex}=350 nm) (**Py-TPE** =20 μM, **WP5**=2 μM, **SR101**= 0.13 μM).

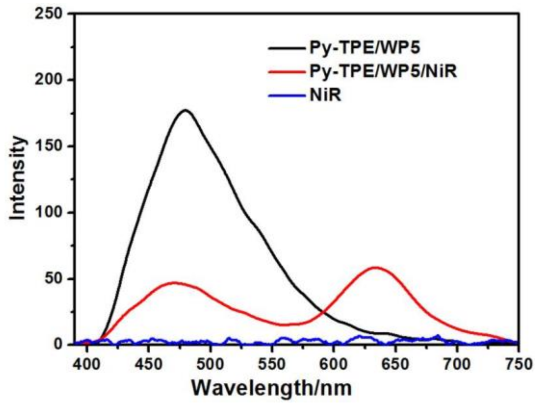
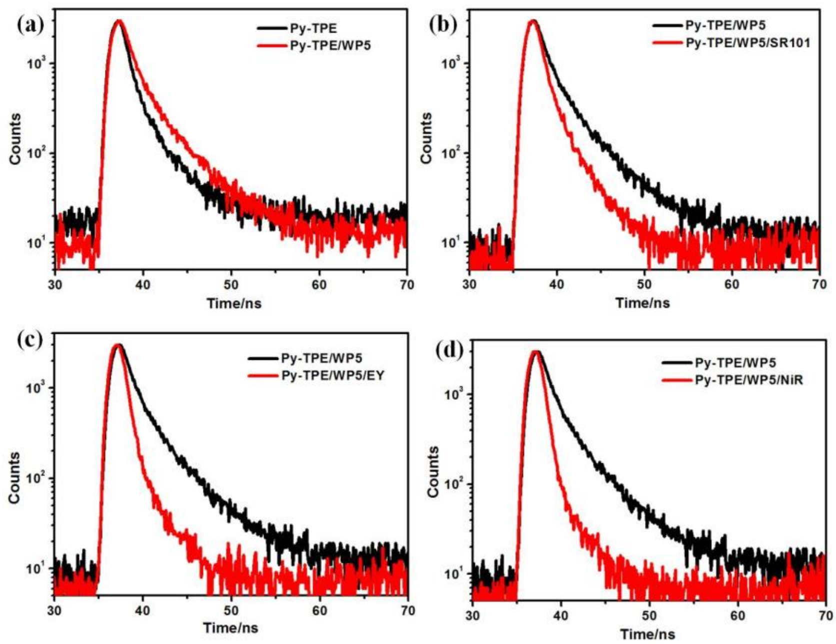


Fig S11. Fluorescence spectra of **Py-TPE/WP5**, **Py-TPE/WP5/NiR** and **NiR** in water (λ_{ex}=350 nm) (**Py-TPE** =20 μM, **WP5**=2 μM, **SR101**= 0.13 μM).



sample	Lifetime(ns)(% contribution)			
	τ1	τ2	τ	χ^2
G	0.93(66.94%)	3.44(33.06%)	1.75ns	1.163
G/WP5	1.10(37.35%)	3.85(62.65%)	2.82ns	1.131
G/WP5/SR101	0.86(63.28%)	2.80(36.72%)	1.57ns	1.187
G/WP5/EY	0.58(61.91%)	2.41(38.09%)	1.27ns	1.309
G/WP5/NiR	0.54(64.58%)	2.67(35.42%)	1.28ns	1.391

Fig S12. The fluorescence lifetime of **Py-TPE**, **Py-TPE/WP5**, **Py-TPE/WP5 /SR101**, **Py-TPE/WP5/EY**, **Py-TPE/WP5/NiR** (λ_{ex}=350 nm, **Py-TPE**=20 μM, **WP5**=2 μM, **SR101**= **EY**=**NiR**=0.13 μM).

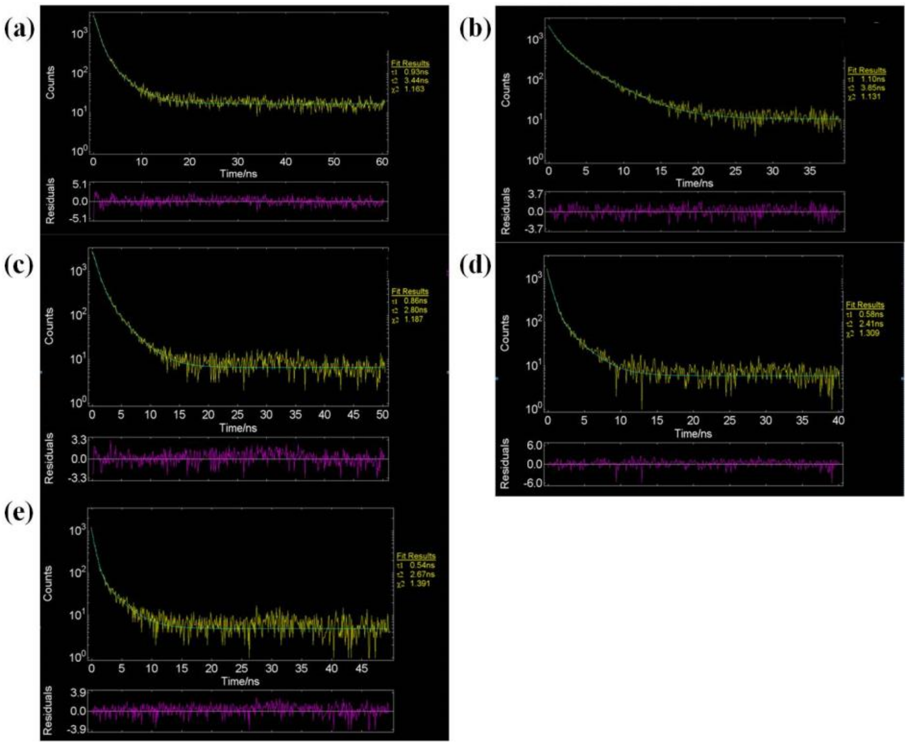


Fig S13. Fluorescence decay traces of (a)**Py-TPE**, (b) **Py-TPE/WP5**, (c)**Py-TPE/WP5/SR101**, (d) **Py-TPE/WP5/EY**, (e) **Py-TPE/WP5/NiR** (**Py-TPE**=20 μM, **WP5**=2 μM, **SR101**= **EY**=**NiR**=0.13 μM).

5. Calculations of energy-transfer efficiency (Φ_{ET}), antenna effect

5.1 Energy-transfer efficiency (Φ_{ET})

Energy-transfer efficiency, Φ_{ET}, the fraction of the absorbed energy that is transferred to the acceptor is experimentally measured as a ratio of the fluorescence intensities of the donor in the absence and presence of the acceptor (I_D and I_{DA}).[2]

$$\Phi_{ET}=1-I_{DA}/I_D$$

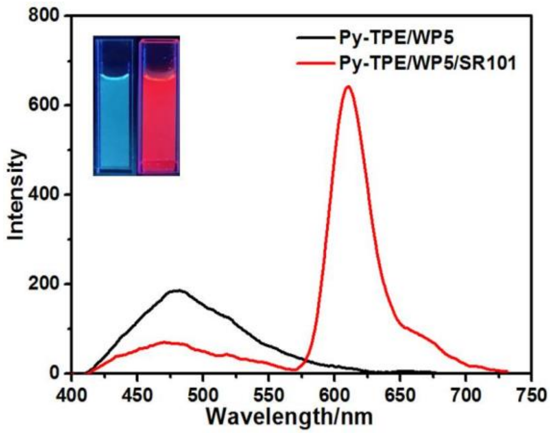


Fig S14. Fluorescence spectra of **Py-TPE/WP5** and **Py-TPE/WP5/SR101** in water (λ_{ex}=350 nm). Inset: photographs of **Py-TPE/WP5** and **Py-TPE/WP5/SR101** under UV light (365 nm) (**Py-TPE** =20 μM, **WP5**=2 μM, **SR101**= 0.13 μM).

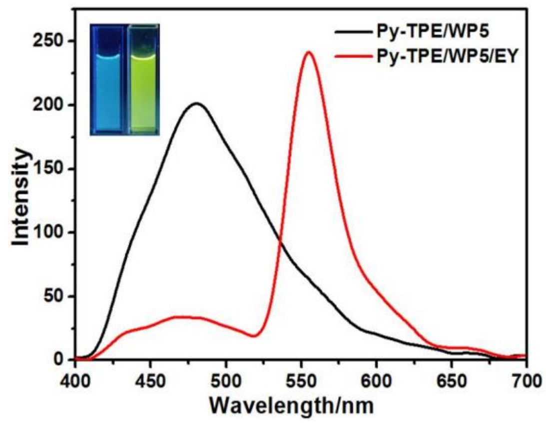


Fig S15. Fluorescence spectra of **Py-TPE/WP5** and **Py-TPE/WP5/EY** in water (λ_{ex}=350 nm). Inset: photographs of **Py-TPE/WP5** and **Py-TPE/WP5/EY** under UV light (365 nm) (**Py-TPE** =20 μM, **WP5**=2 μM, **EY** = 0.13 μM).

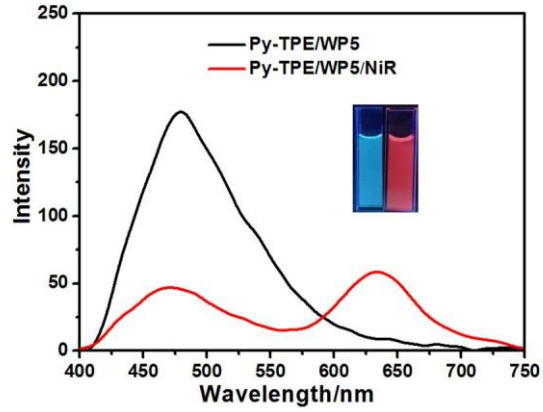


Fig S16. Fluorescence spectra of **Py-TPE/WP5** and **Py-TPE/WP5/NiR** in water (λ_{ex}=350 nm). Inset: photographs of **Py-TPE/WP5** and **Py-TPE/WP5/ NiR** under UV light (365 nm) (**Py-TPE** =20 μM, **WP5**=2 μM, **NiR** = 0.13 μM).

5.2 Antenna effect

The antenna effect under certain concentrations of donor and acceptor equals the ratio of the emission of the acceptor upon excitation of the donor.[2]

$$\text{Antenna effect} = I_{A+D(\lambda ex=donor)} - I_{D(\lambda ex=donor)} / I_{A+D(\lambda ex=acceptor)}$$

Where I_{A+D} (λ_{ex} = donor) and I_{A+D} (λ_{ex} =acceptor) are the fluorescence intensities of excitation of the donor and direct excitation of the acceptor, respectively. I_D (λ_{ex}= donor) is the fluorescence intensities of the **Py-TPE/WP5** assembly, which was normalized with the **Py-TPE/WP5/acceptor** assembly at 480 nm.

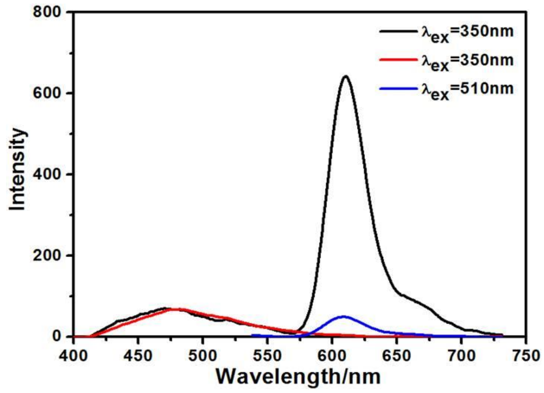


Fig S17. Fluorescence spectra of **Py-TPE/WP5/SR101** in water, black trace (donor emission, λ_{ex} = 350 nm), blue trace (acceptor emission, λ_{ex} = 510 nm). The red trace represents the fluorescence spectrum (λ_{ex}=350 nm) of **Py-TPE/WP5**, which was normalized according to the fluorescence intensity at 480 nm of the black trace (**Py-TPE** =20 μM, **WP5**=2 μM, **SR101**= 0.13 μM).

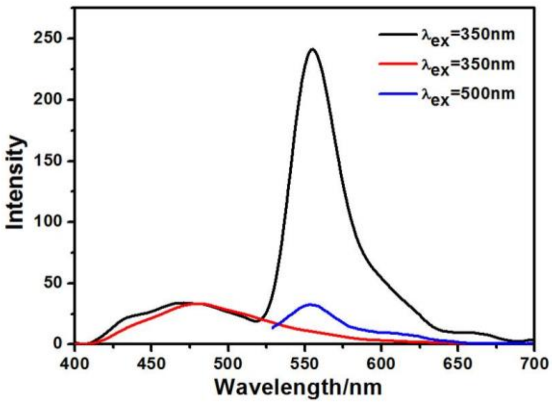


Fig S18. Fluorescence spectra of **Py-TPE/WP5/EY** in water, black trace (donor emission, λ_{ex} = 350 nm), blue trace (acceptor emission, λ_{ex} = 500 nm). The red trace represents the fluorescence spectrum (λ_{ex}=350 nm) of **Py-TPE/WP5**, which was normalized according to the fluorescence intensity at 480 nm of the black trace (**Py-TPE** =20 μM, **WP5**=2 μM, **EY**= 0.13 μM).

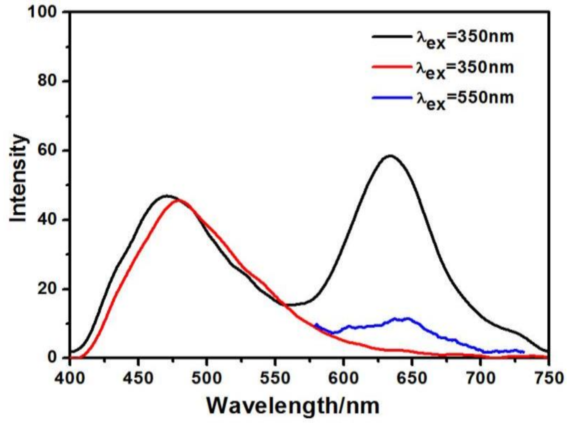


Fig S19. Fluorescence spectra of **Py-TPE/WP5/NiR** in water, black trace (donor emission, λ_{ex} = 350 nm), blue trace (acceptor emission, λ_{ex} = 550 nm). The red trace represents the fluorescence spectrum (λ_{ex}=350 nm) of **Py-TPE/WP5**, which was normalized according to the fluorescence intensity at 480 nm of the black trace (**Py-TPE** =20 μM, **WP5**=2 μM, **NiR** = 0.13 μM).

6. **Construction and characterization of two-step sequential energy transfer in aqueous solution**

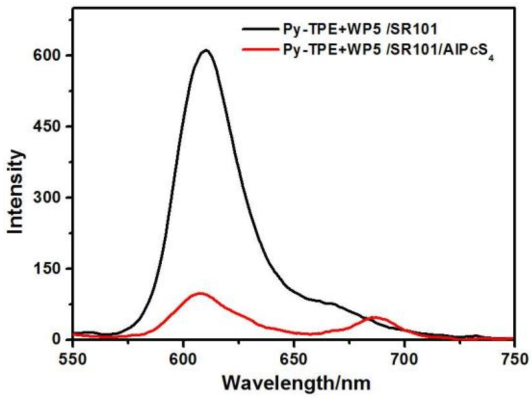


Fig S20. Fluorescence spectra of **Py-TPE/WP5/SR101** and **Py-TPE/WP5/ SR101/AlPcS$_4$** in water (λ_{ex}=350 nm) (**Py-TPE** =20 μM, **WP5**=2 μM, **SR101**= 0.13 μM, **AlPcS$_4$**=0.015 μM)..

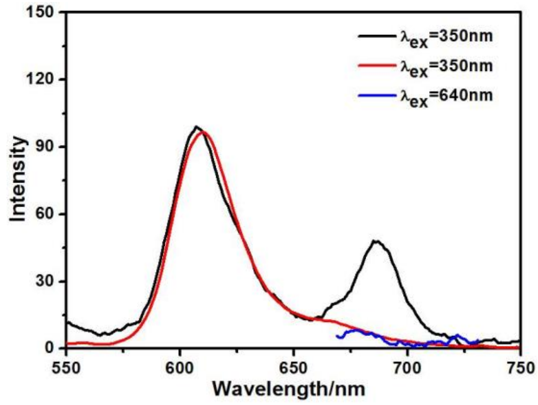
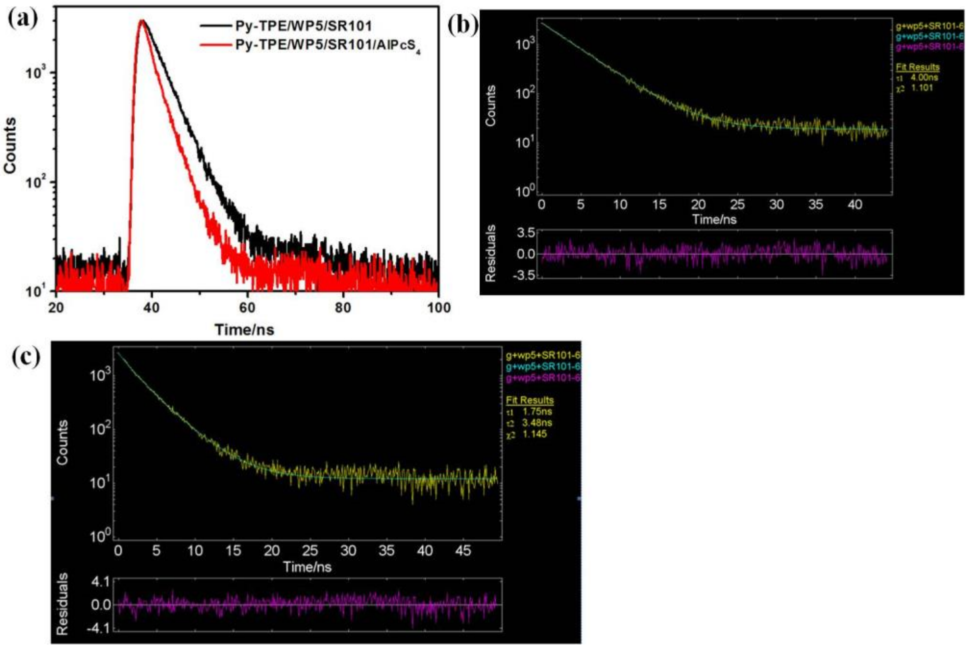


Fig S21. Fluorescence spectra of **Py-TPE/WP5/SR101/AlPcS$_4$** in water, black trace (donor emission, λ_{ex} = 350 nm), blue trace (acceptor emission, λ_{ex} = 640 nm). The red trace represents the fluorescence spectrum (λ_{ex}=350 nm) of **Py-TPE/WP5/SR101**, which was normalized according to the fluorescence intensity at 610 nm of the black trace (**Py-TPE** =20 μM, **WP5**=2 μM, **SR101**= 0.13 μM, **AlPcS$_4$**=0.015 μM).



(d)

sample	Lifetime(ns)(% contribution)			
	τ1	τ2	τ	χ^2
G/WP5/SR101	4.03(100%)		4.03ns	1.101
G/WP5/SR101/AlPcS$_4$	1.75(28.17%)	3.48(71.83%)	2.99ns	1.145

Fig S22. (a) (d) The fluorescence lifetime of **Py-TPE/WP5/SR101** and **Py-TPE/WP5/SR101/AlPcS$_4$**. Fluorescence decay traces of **SR101** in (b) **Py-TPE/WP5/SR101** and (c) **Py-TPE/WP5/SR101/AlPcS$_4$** supramolecular assembly. (**Py-TPE**=20 μM, **WP5**=2 μM, **SR101**= 0.13 μM, **AlPcS$_4$**=0.015 μM).

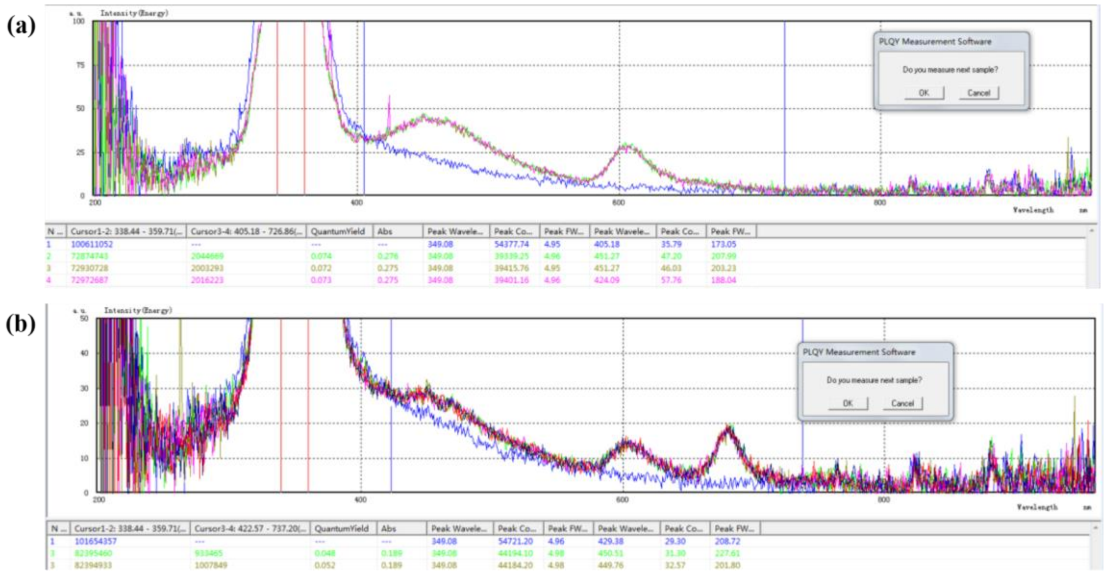


Fig S23. (a) The fluorescence quantum yield of **Py-TPE/WP5/SR101** assembly; (b)The fluorescence quantum yield of **Py-TPE/WP5/SR101/AlPcS$_4$** assembly.

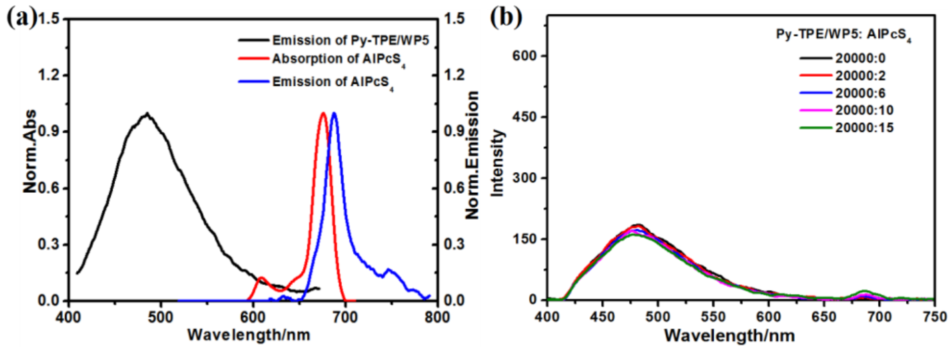


Fig S24. (a) Normalized emission spectrum of **Py-TPE/WP5**, absorption and emission spectrum of **AlPcS$_4$**. (b) Fluorescence spectrum of Py-TPE/WP5 in water with different concentrations of AlPcS$_4$. ([**Py-TPE**] = 20 μM, [**WP5**] = 2 μM) The concentrations of **AlPcS$_4$** were 0.00 μM, 0.002 μM, 0.006 μM, 0.01 μM, 0.015 μM,

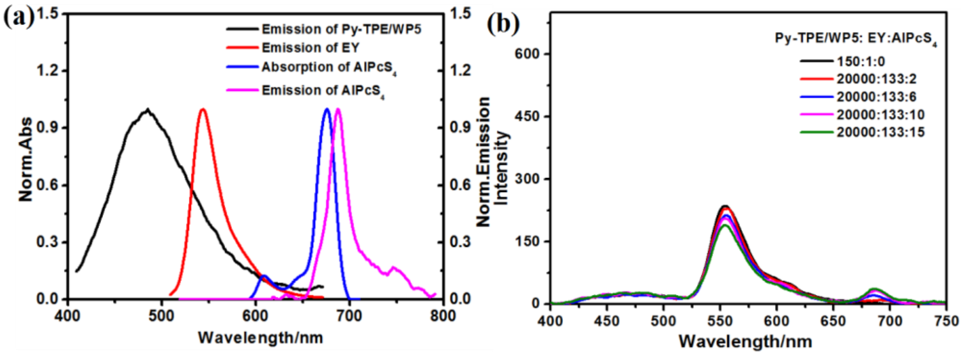


Fig S25. (a) Normalized emission spectrum of **Py-TPE/WP5** and **EY**, absorption and emission spectrum of **AlPcS$_4$**. (b) Fluorescence spectrum of **Py-TPE/WP5/EY** ([**Py-TPE**] = 20 μM, [**WP5**] = 2 μM, [**EY**] = 0.13 μM) in water with different concentrations of **AlPcS$_4$**. The concentrations of **AlPcS$_4$** were 0.00μM, 0.002 μM, 0.006 μM, 0.01 μM, 0.015 μM.

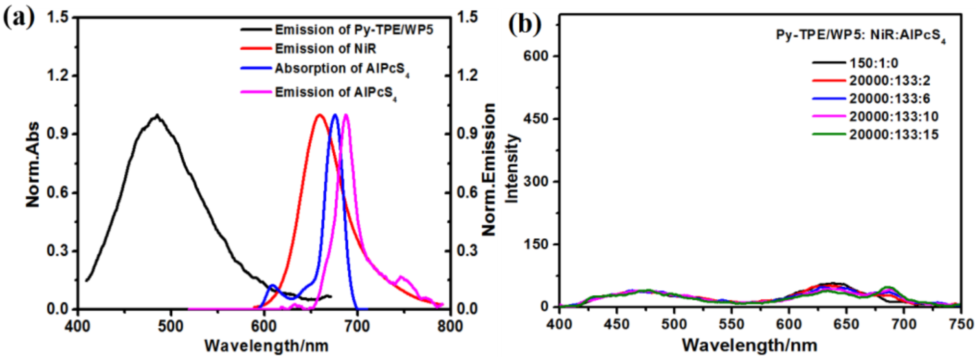


Fig S26. (a) Normalized emission spectrum of **Py-TPE/WP5** and **NiR**, absorption and emission spectrum of **AlPcS$_4$**. (b) Fluorescence spectrum of **Py-TPE/WP5/NiR** ([**Py-TPE**] =20 μM, [**WP5**] = 2 μM, [**NiR**] = 0.13 μM) in water with different concentrations of **AlPcS$_4$** .The concentrations of **AlPcS$_4$** were 0.00μM, 0.002 μM, 0.006 μM, 0.01 μM, 0.015 μM.

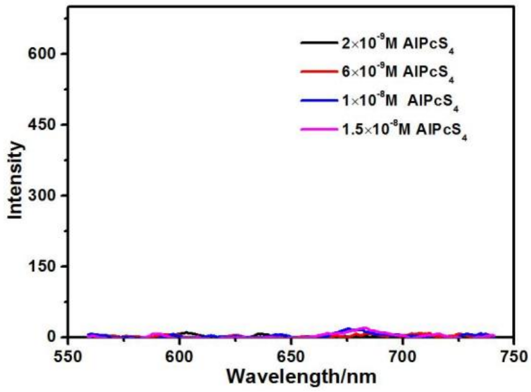


Fig S27. Fluorescence spectrum of **AlPcS$_4$** in different concentration.

References:

1. Y. Guo, D. Shi, Z. W. Luo, J. R. Xu, M. L. Li, L. H. Yang, Z. Q. Yu, E. Q. Chen, H. L. Xie, *Macromolecules*. 2017, **50**, 9607.
2. (a) J. J. Li, Y. Chen, J. Yu, N. Cheng, Y. Liu, *Adv. Mater.* 2017, **29**, 1701905; (b) S. Guo, Y. Song, Y. He, X. Y. Hu, L. Wang, *Angew. Chem. Int. Ed.* 2018, **57**, 3163; (c) M. Hao, G. P. Sun, M. Z. Zuo, Z. Q. Xu, Y. Chen, X. Y. Hu, L. Y. Wang, *Angew. Chem. Int. Ed*. 2019, **58**, 2.