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Supporting Information

Stable highly-efficient white-light emission from panchromatic luminescent aldehyde-based diphenylanthracene derivatives doped with triplet sensitizer

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1. Measurements.

Melting point was measured using a YUHUA X-5 micro melting point tester. UV absorption spectra was measured on the SHIMADZU uv-2600 UV-visible absorption spectrometer. IR spectra were obtained on Thermo Fisher Nicolet iS5. Element analyses were performed on German ELEMENTAR element analyzer (vario micro). ^{1}H NMR and ^{13}C NMR were performed on an INOVA-400 spectrometer in DMSO-d_6 as solvent. Mass spectra were obtained on Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS) produced by Bruker Company (bruker solarix X).

For the white-light measurements via the upconversion approach, the annihilator/sensitizer pair both in solution (DMSO) and in polymer matrix were excited by the diode solid state laser (532 nm). The obtained emission spectra were recorded with PR655 Spectra Scan colorimeter and the white-light efficiency (Φ_{WL}) was calculated by *Eqn*. (1).

$$\Phi_{\mathrm{WL}} = 2\Phi_{\mathrm{r}}\left(\frac{A_r}{A_s}\right)\left(\frac{\mathrm{F}_s}{\mathrm{F}_r}\right)\left(\frac{\eta_s}{\eta_r}\right)^2 \qquad (1)$$

For the white-light emission efficiency in solution, the parameters A_r and A_s are the absorbance of the reference (rhodamine 6G, Rh6G) and sample (sensitizer PdBrTPP), respectively. While F_s and F_r are the integral areas of emission spectra of sample (annihilator) and reference (Rh6G), respectively. Φ_r is the fluorescence quantum yield of Rh6G (88% in EtOH). η_s and η_r are the refractive indexes of sample solution and reference solution, respectively. Here, η_s and η_r are approximately the refractive indexes of

DMSO and EtOH, respectively. The parameters based on the *Eqn.* (1) for three sensitizer-annihilator pairs in solution and reference (Rh6G solution) are presented in Table S2.

For the white-light emission efficiency in polymer, the parameters A_s is the absorbance of PdBrTPP in polymer. F_s is the integral area of emission spectra of annihilator in polymer. η_s is the refractive index of blank polymer (2-hydroxyethylmethacrylate). Noted that the parameters A_s and F_s in polymer matrix are obtained from the polymer materials with 2-cm thick, as shown in Table S2. For the calculation of white-light efficiency in polymer, Rh6G (in ethanol) was still chosen as the standard reference.

It's important to point out that under the UC excitation approach (i.e., 532 nm green laser excitation), the distinction between the calculations of white-light efficiency and the usual green-to-blue upconversion efficiency only lies in the F_s values. As shown in the *Eqn.* (1), the F_s value for the white-light efficiency is obtained by integrating the area of the whole visible spectrum (400~780 nm) of annihilator; while the F_s value for the green-to-blue efficiency is obtained by integrating the area of blue-light region (400~520 nm) of annihilator. Meanwhile, Rh6G was chosen as the standard reference since its fluorescence quantum yield was known (in ethanol solution, 88%) under the excitation of 532 nm that is the same as the excitation wavelength used in this paper.

Thus, the parameters to calculate white-light efficiency, involved in *Eqn.* (1) for sensitizer-annihilator pairs (PdBrTPP- **HPFPA** and PdBrTPP-**FPCPA**) and doped polymer as well as grafting polymer are presented in **Table S2**, according to **Fig. S22~ S25**. The obtained white-light emission efficiency (Φ_{WL}) were calculated and also presented in **Table S2**.

2. Synthesis and Characterization

(1) 9,10-*di*(4'-formylphenyl)anthracene (**DFPA**): Under the argon atmosphere, a mixture of 4-formylbenzenboric acid (2.82 g, 2.5 equiv, 18.8 mmol) and 9, 10-dibromoanthracene (2.53 g, 1 equiv, 7.5 mmol) were added to the three-necked flask in presence of 60 mL of toluene and 12 mL of ethanol. Then, K_2CO_3 aqueous solution (5.92 g, 34.5 mmol in 23 mL distilled water) was added into the above solution. After blowing Ar gas for 15 minutes, 0.25 g of tetrakis (triphenylphosphine) palladium (0) (0.82 mmol) was added and then refluxing reaction in the argon atmosphere. The reaction progress is tracked through TLC tracking, and the mobile phase was dichloromethane/petroleum ether (1/1, v/v). After reaction for 48 h, the point of 9, 10-dibromanthene almost disappeared and the reaction stopped. After decompression distillation of the reaction solution, black solid mixture was obtained. Dichloromethane and saturated salt water were selected for multiple extraction to separate the organic phase. Anhydrous Na_2SO_4 was added to remove water. Column chromatography was used to separate the products. The mobile phase used was dichloromethane/petroleum ether (3/4, v/v). After recrystallization and secondary purification by solvent evaporation, the white powder of 9, 10-*di*(4’-formylphenyl)anthracene (**DFPA**) was obtained (1.84 g, yield 64.3%, mp: 378.2 ℃). Anal. Calcd (%) for $C_{28}H_{18}O_2$: C, 87.02; H, 4.69. Found: C, 87.31; H, 4.61. MS (MALDI-TOF): Calcd. 387.1385 [M^{+}+H]; Found 387.1373 (**Fig. S1**). ^{1}H NMR (400 MHz, Chloroform-*d*) δ= 7.39-7.51 (m, 8H), 7.55-7.64 (d, *J* = 7.4 Hz, 2H), 7.81-7.91 (t, *J* = 7.7 Hz, 2H), 7.93-8.04 (t, *J* = 7.5 Hz, 2H), 8.15- 8.21 (d, *J* = 8.5 Hz, 2H), 9.33-9.40 (s, 2H) (**Fig. S2**).

(2) 9,10-*di*(4’-hydroxymethylphenyl)anthracene (DHMPA): A mixture of 9, 10-*di*(4’-formylphenyl)anthracene (**DFPA**) (1.16 g, 3 mmol) and KBH_4 (432 mg, 8 mmol) was added to a single-necked flask in the presence of ethanol (20 mL). The reaction was then stirred at room temperature for 24 h. After the reaction was completed, the reaction solution was poured into a large amount of distilled water, stirred well, and suction filtered, respectively. The residue was repeatedly washed with distilled water and placed in a vacuum drying oven to dry at 60°C. After recrystallization from $CHCl_3$, a white powders of 9,10-*di*(4’-hydroxymethylphenyl)anthracene (**DHMPA**) was obtained (0.85 g, yield 72.8%, mp: 314.5℃). Anal. Calcd (%) for $C_{28}H_{22}O_2$: C, 86.13; H, 5.68. Found: C, 86.11; H, 5.61. MS (MALDI-TOF): Calcd. 391.1698 [M^{+}+H]; Found 391.1691 (**Fig. S3**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.60-4.72 (d, *J*=5.8 Hz, 4H), 5.28-5.40 (td, *J*=5.8, 1.4 Hz, 2H), 7.25-7.38 (d, *J*=7.4 Hz, 2H), 7.39-7.51 (dd, *J*=11.2, 5.0, 2.4 Hz, 6H), 7.50-7.69 (m, 8H) (**Fig. S4**).

(3) 9,10-*di*(4’-carboxylphenyl)anthracene (DCPA): A mixture of 9, 10-*di*(4’-formylphenyl)anthracene (**DFPA**) (1 g, 2.6 mmol) and $KMnO_4$ (4.5 g, 28.5 mmol) was dissolved in THF (20 mL) and stirred at room temperature for 72 h. The reaction mixture was washed with 500 ml of THF and then filtered to give filtrate and concentrated. The crude product was vacuum dried and purified by column chromatography with ethyl acetate/dichloromethane (1/2, v/v) as the eluent. After crystalization, white powder of **DCPA** was obtained (0.41 g, yield: 40%, mp: 328.4℃). Anal. Calcd (%) for $C_{28}H_{18}O_4$: C, 80.37; H, 4.34. Found: C, 80.11; H, 4.51. MS (MALDI-TOF): Calcd. 418.1205; Found 418.1199 (**Fig. S5**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.47-7.63 (m, 14H), 8.22-8.24 (d, *J*=8 Hz, 4H), 13.19 (s, 2H) (**Fig. S6**).

(4) 9-(4-Hydroxymethylphenyl)-10-(4’-formylphenyl) anthracene (HPFPA): The aqueous solutions of **DFPA** (1.16g, 3 mmol) and KBH_4 (0.35g, 6.5 mmol) were dissolved in 20 mL ethanol and stirred for 24 h at room temperature. After the reaction was over, the reaction liquid was cooled to room temperature, and a large amount of distilled water was poured to precipitate and filter. The crude product was vacuum dried and purified by column chromatography with eluent as ethyl acetate/petroleum ether (1/2, v/v). Bright yellow powder product **HPFPA** was obtained (0.50 g, yield: 43.1%, mp: 348.6°C). Anal. Calcd (%) for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19. Found: C, 86.51; H, 5.11. MS (MALDI-TOF): Calcd. 388.1463; Found 388.1463 (Mz) (**Fig. S7**). ^1H NMR (400 MHz, DMSO-d_6): δ=10.23 (s, 1H), 8.26-8.16 (m, 2H), 7.77-7.70 (m, 2H), 7.68-7.61 (m, 4H), 7.57-7.48 (m, 2H), 7.46-7.36 (m, 6H), 5.36 (s, 1H), 4.71 (s, 2H) (**Fig. S8**). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 187.82, 136.70, 136.19, 136.09, 132.42, 131.10, 130.28, 129.72, 129.31, 127.23, 127.06, 126.47, 126.38, 126.03, 63.30. (**Fig. S9**). ν (KBr)/cm^{-1}: 3452.50 (O-H), 3062.28 (C-H), 2923.87 ($-CH_2-$), 2855.04 ($-CH_2-$), 2728.81 (-CHO), 1696.64 (aromatic -CHO), 1600.77 (Ar-), 1206.36 (C-O), 815.86 (aromatic C-H), 767.65 (aromatic C-H), 668.78 (C-H) (**Fig. S10**).

(5) 9-(4-Formylphenyl)-10-(4'-carboxylphenyl) anthracene (FPCPA): The intermediate 9, 10-bis (4-formylphenyl) anthracene (**DFPA**, 1 g, 2.6 mmol) and $KMnO_4$ (4.5 g, 28.5 mmol) were dissolved in 20 mL ethanol and stirred at room temperature for 24 h. Stay after the reaction, the reaction liquid was cooled to room temperature, then pumped and filtered with 40 ml methylene chloride of washing. The filtrate was poured into a large amount of distilled water to precipitate and then pumped for filtration. The crude product was vacuum dried and purified by column chromatography (the eluent was ethyl acetate/dichloromethane =1/4, v/v), and light yellow powder product **FPCPA** was obtained (0.4 g, yield: 40%, mp: 384.7°C). Anal. Calcd (%) for $C_{28}H_{18}O_3$: C, 83.57; H, 4.51. Found: C, 83.50; H, 4.41. MS (MALDI-TOF): Calcd. 402.1256; Found 402.1253 (**Fig. S11**). ^1H NMR (400 MHz, DMSO-d_6): δ=13.17 (s, 1H), 10.23 (s, 1H), 8.22 (t, *J*=8.4 Hz, 4H), 7.75 (d, *J*=8.0 Hz, 2H), 7.65-7.42 (m, 10H) (**Fig S12**). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 193.49, 167.70, 145.10, 143.26, 136.14, 132.37, 131.75, 130.30, 130.13, 129.34, 129.26, 126.56, 126.50, 126.43. (**Fig. S13**). ν (KBr)/cm^{-1}: 3450.03 (O-H), 2922.85 (carboxyl O-H), 2853.23 (carboxyl O-H), 1694.51 (aromatic -CHO), 1461.40 (Ar-), 824.90 (C-H), 767.48 (C-H), 669.14 (C-H) (**Fig. S14**).

(6) FPCPA/PdBrTPP (1 mM/4μM) jointly doped polymer (abbreviated as doped polymer**):** 0.8 mL (6.6 mmol) of monomer *2*-hydroxyethylmethacrylate (HEMA) was mixed with 0.8 mL of **FPCPA** solution (2 mM, DMSO) in the presence of azobisisobutyronitrile (AIBN, 0.5 wt%) as initiator. Then 6.4

μL of PdBrTPP solution (1 mM, bromobenzene as solvent) was added to the above mixtures. The reaction mixture was placed in a conventional oven at 45°C for 2h and 75℃ for 5h, respectively. The obtained transparent doped polymer was then cooled to room temperature and stored in the dark for the measurements.

(7) The PdBrTPP-doped **FPCPA-**grafting polymer **(**abbreviated as grafting polymer poly(**FPCPA-**HEMA) was prepared by the reaction of 2-hydroxyethylmethacrylate (HEMA) and **FPCPA** via the esterification and in situ polymerization. The concentration of **FPCPA/PdBrTPP** are at (1 mM/4μM). The procedure is as follows:

0.8 mL (6.6 mmol) of monomer *2*-hydroxyethylmethacrylate (HEMA) was mixed with 0.8 mL **FPCPA** solution (2 mM, DMSO) in the presence of azobisisobutyronitrile (AIBN, 0.5 wt%) as initiator and N,N'-dicyclohexylcarbodiimide (**DCC**, 0.4 mg) as the dehydrator. Then 6.4 μL PdBrTPP solution (1 mM, bromobenzene as solvent) was added to the above monomer mixtures. The above mixture solution was sonicated for 15 minutes to be sufficiently dissolved and mixed. The reaction mixture was placed in a conventional oven at 45°C for 2h and 75℃ for 5h, respectively. The obtained transparent doped polymer was then cooled to room temperature and stored in the dark for the measurements.

IR spectrum of the grafted polymer, poly-(FPCPA-HEMA) was measured. For comparison, IR spectrum of the blank sample, poly-HEMA, was also presented (**Fig. S15**). It was found that a weak peak at 1635.34 cm^{-1} could be recognized, which is assigned to stretching vibration of aldehyde group (CHO). Since the grafted concentration of FPCPA (annihilator) in HEMA (monomer) is very low (1.2×10^{-4} mol/L), this peak is not strong. In addition, we noticed that there are obvious differences in the fingerprint region between poly-HEMA and poly-(FPCPA-HEMA). The peaks at 748.22 cm^{-1} and 700.02 cm^{-1} can be attributable to the disubstituted benzene vibration.

However, the molecular weight of these polymers cannot be analyzed by GPC measurement, since they are insoluble in almost all of solvents, such as toluene, CH_2Cl_2, $CHCl_3$, THF, DMF, DMSO, HFIP (hexafluoroisopropanol) and TCB (1,2,4-trichlorobenzene), even under the conditions of grinding and heating. The reason is that the HEMA homopolymerization in this work is the kind of crosslinked hydrogel.[1, 2]

3. Spectral Calculations

In order to understand why only aldehyde-substituted derivatives show the broad-band emission, we used the Gaussian 09[3] and MultiWFN[4] program package to simulate the fluorescence spectra of different chromophores. TD-DFT[5] method was used to optimize the S_1 state configurations of chromophores firstly and PCM[6] method was applied then, representing the solvent surrounding the substances, to examine the solvent effect of DMSO. Thus, the radiation transition probability and the radiation transition distribution simulated by PBE/6-311+G* method are obtained (see Fig. S19).

As shown in Fig. S19 (a~e), there are several vertical lines with different height and differetn discrete distribution. The former stands for the the radiation transition probability of chromophore while the later for the the radiation transition distribution range. That is, the larger discrete degree of vertical lines, the wider fluorescence spectrum. Based on these vertical lines, the fitted fluorescence spectra for different chromophores can be obtained. Clearly, the chromophores with aldehyde group (**HPFPA, FPCPA** and DFPA) exhibit broader band emission with FWHM ~140 nm, while chromophore DHMPA and DCPA (without aldehyde group) present narrower band emission with FWHM ~120 nm, respectively. Further calculations on the absorption spectra were found that the molecules with -CHO group possess extra transition with HOMO-LUMO and HOMO-LUMO+1, shown in Fig. S20 (a~c). The former are mainly concentrated on the orbitals of the anthracene rings, while the LUMO+1 is obviously composed of the orbitals of the -CHO group, indicating that the -CHO group contributes to the absorption at the long wave of the molecule, that is, to the emission broadening. On the other hand, the molecules without -CHO group, their transition mode was obviously restrained at HOMO-LUMO. As shown in Fig. S20 (d, e), the electron cloud change was mainly concentrated on the orbitals of the anthracene rings, while the -COOH and –CH_2OH in the terminal contribute nothing to the front molecular orbitals.

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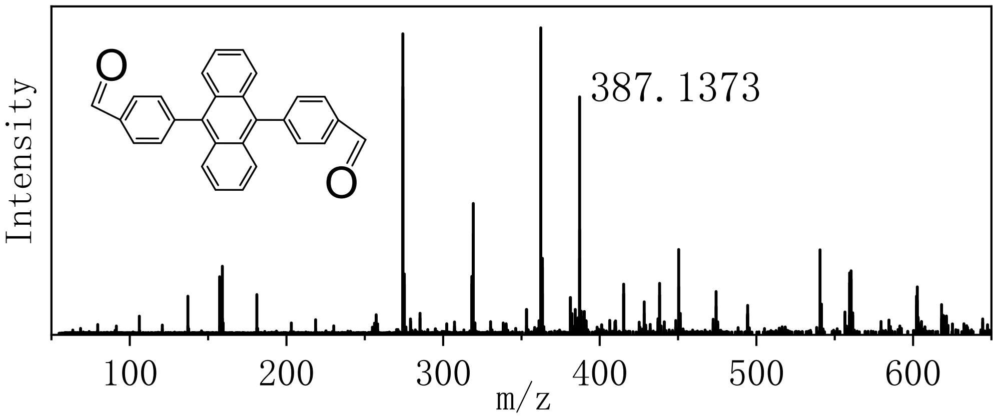


Fig. S1 Mass spectrum of **DFPA** and molecular formula.

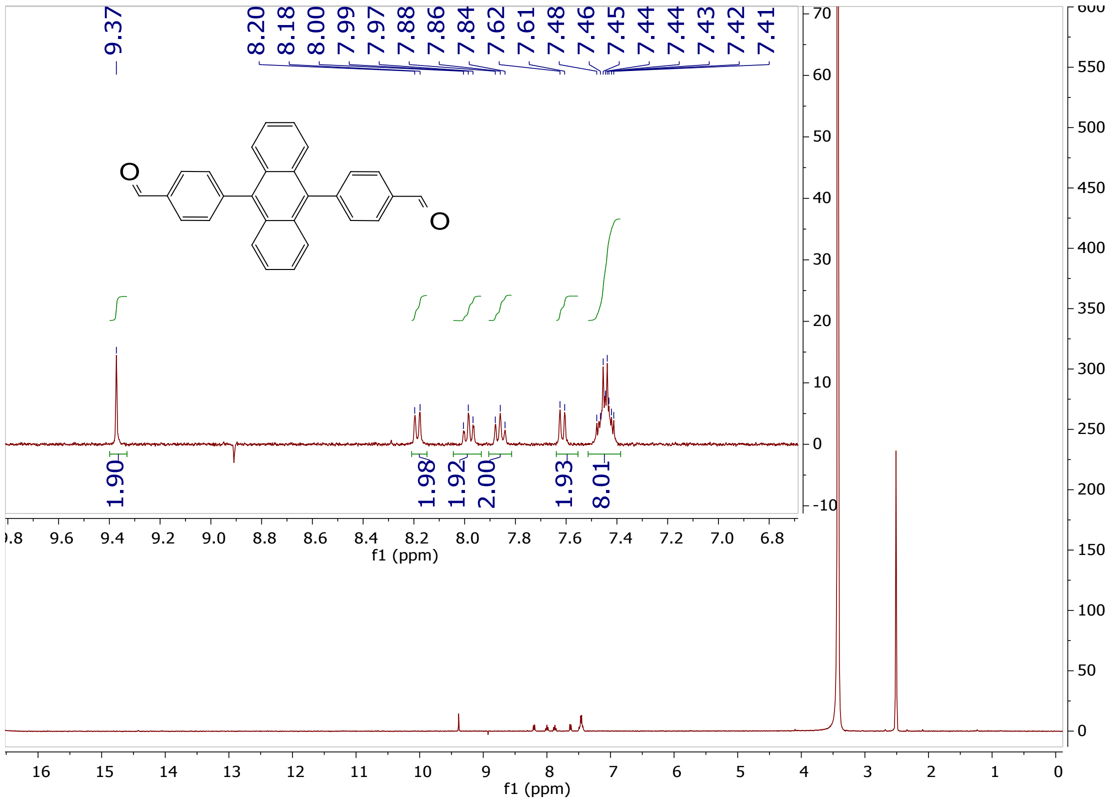


Fig. S2 ^{1}H NMR for **DFPA** (solvent: Chloroform-*d*).

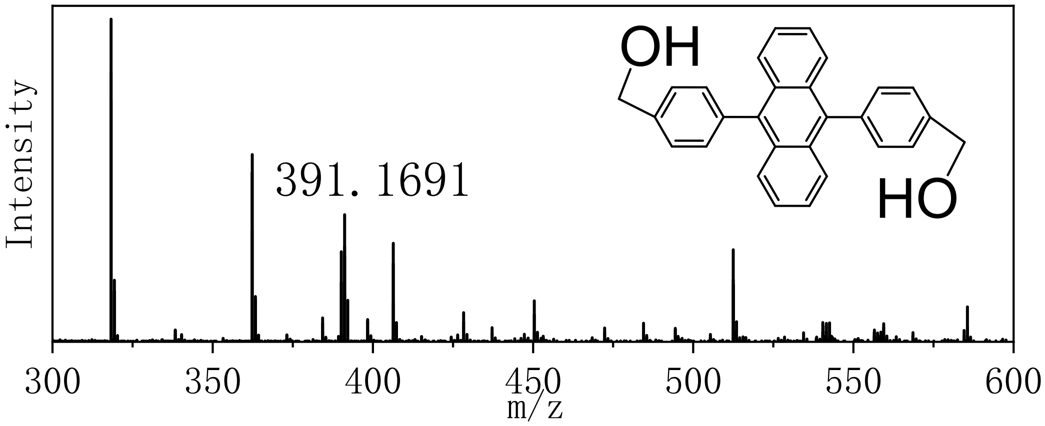


Fig. S3 Mass spectrum of **DHMPA** and molecular formula.

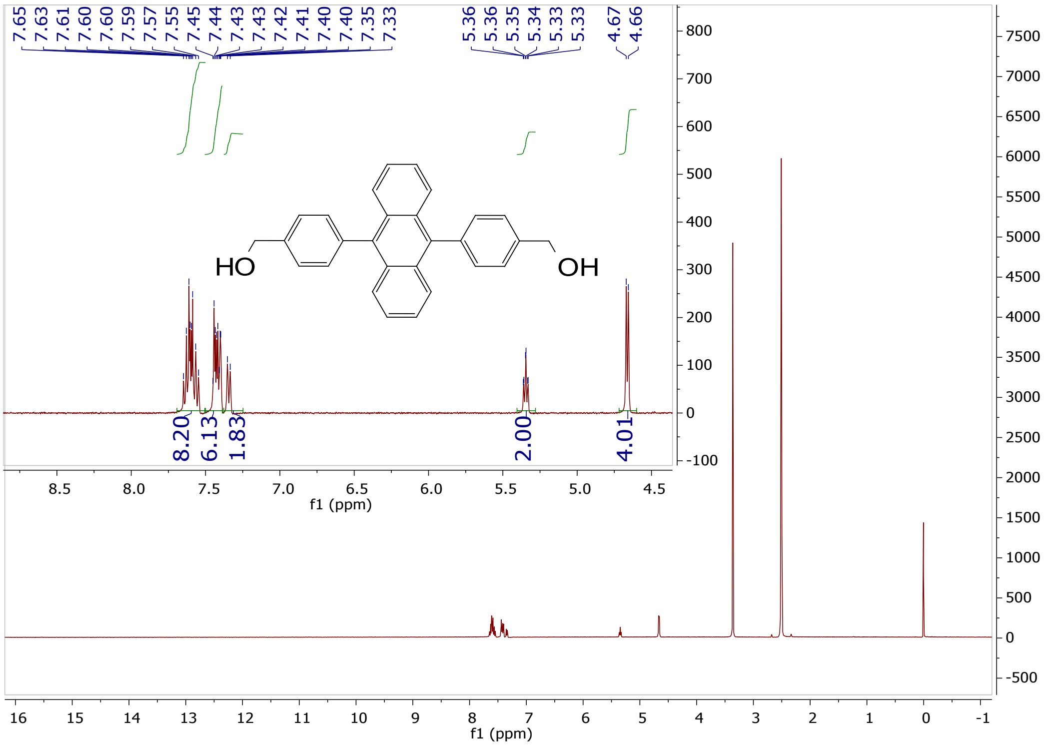


Fig. S4 ^{1}H NMR for **DHMPA** (solvent: DMSO-d_6).

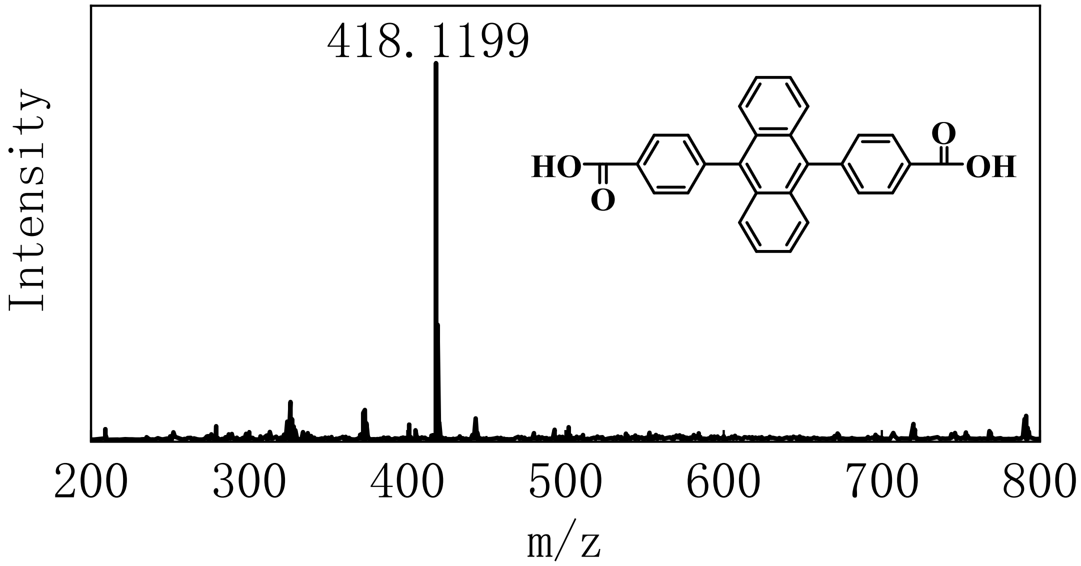


Fig. S5 Mass spectrum of **DCPA** and molecular formula.

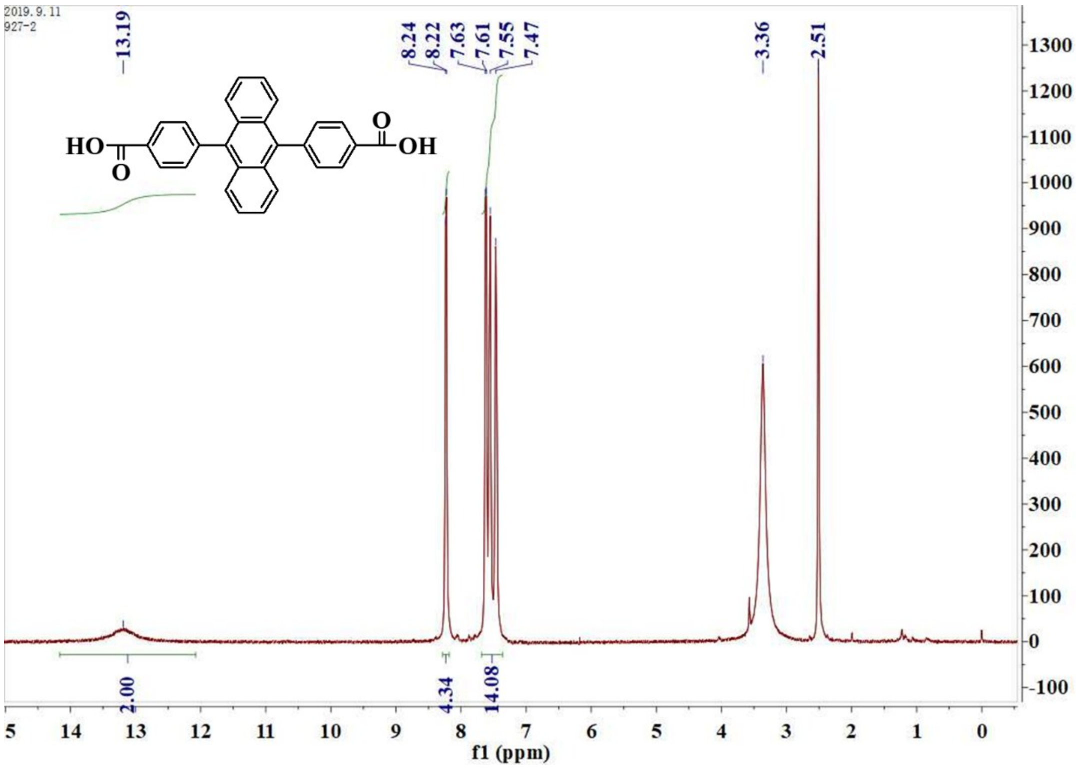


Fig. S6 ^{1}H NMR for **DCPA** (solvent: DMSO-d_6).

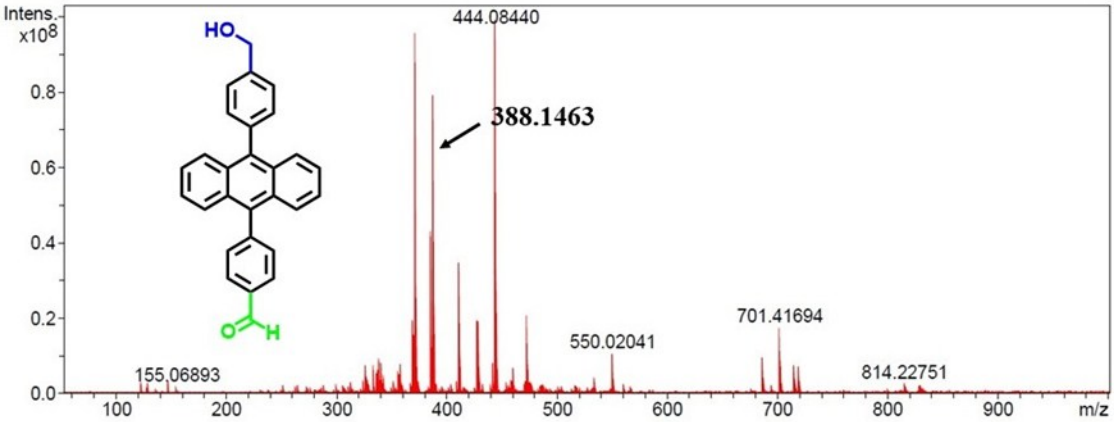


Fig. S7 Mass spectrum of **HPFPA** and molecular formula.

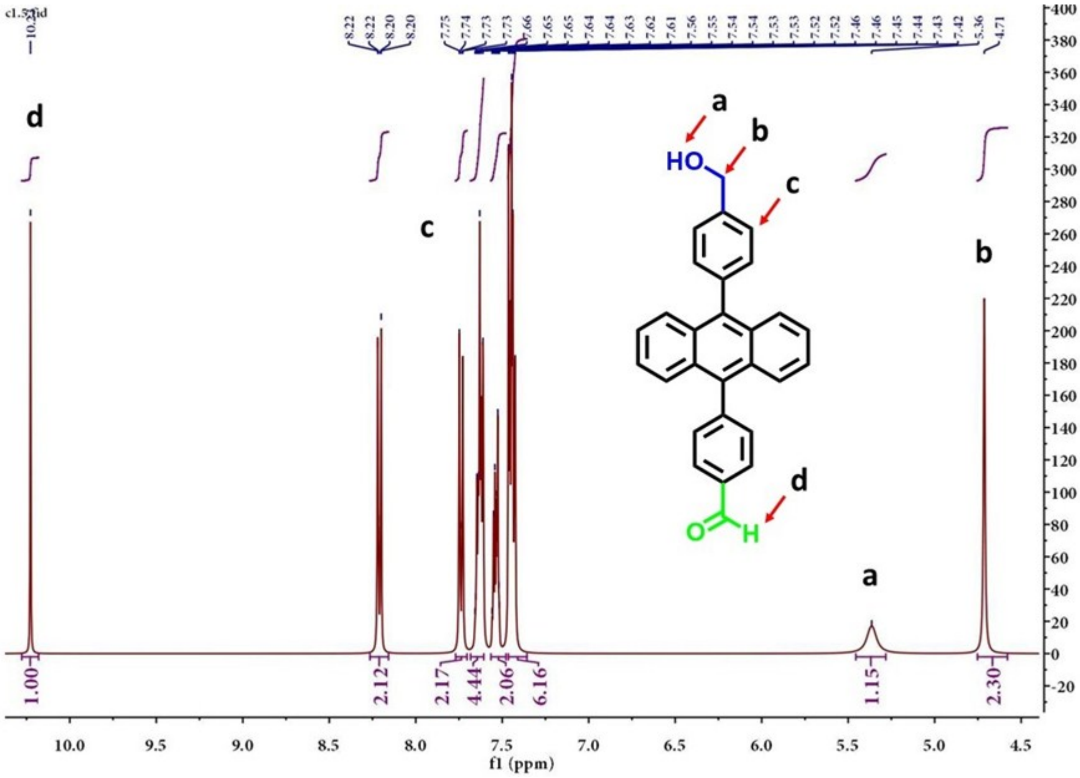


Fig. S8 ^{1}H NMR for **HPFPA** (solvent: DMSO-d$_6$)

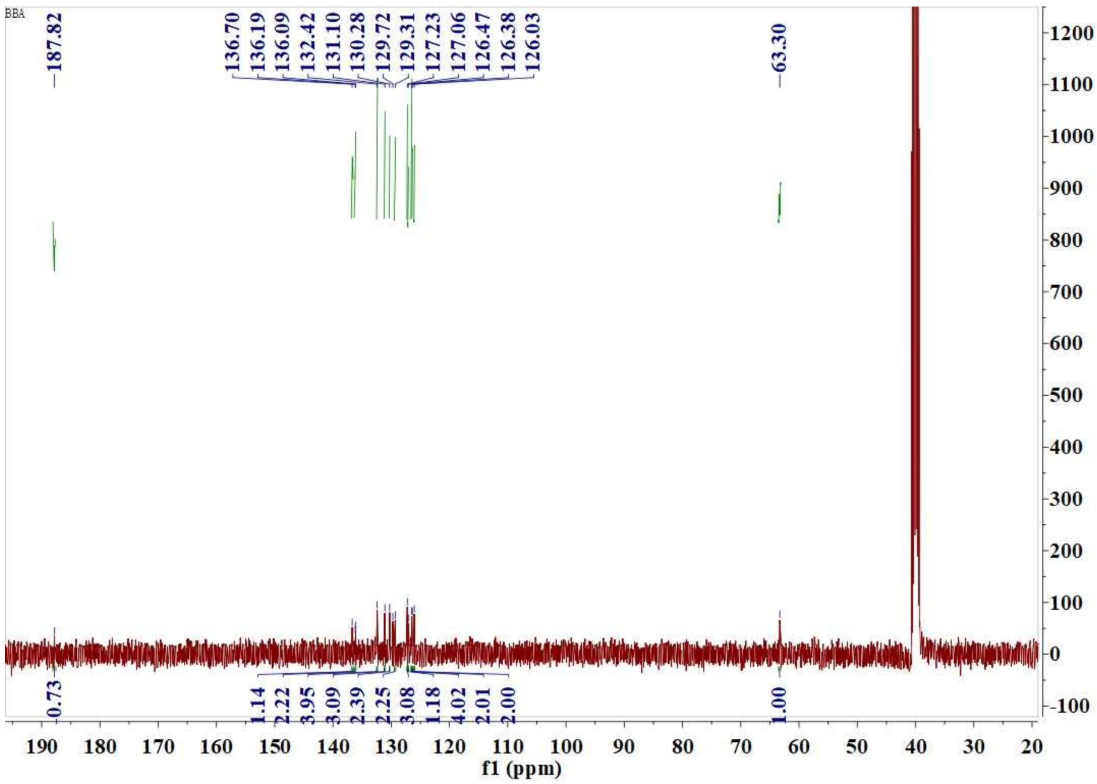


Fig. S9 ^{13}C NMR for **HPFPA** (solvent: DMSO-d$_6$)

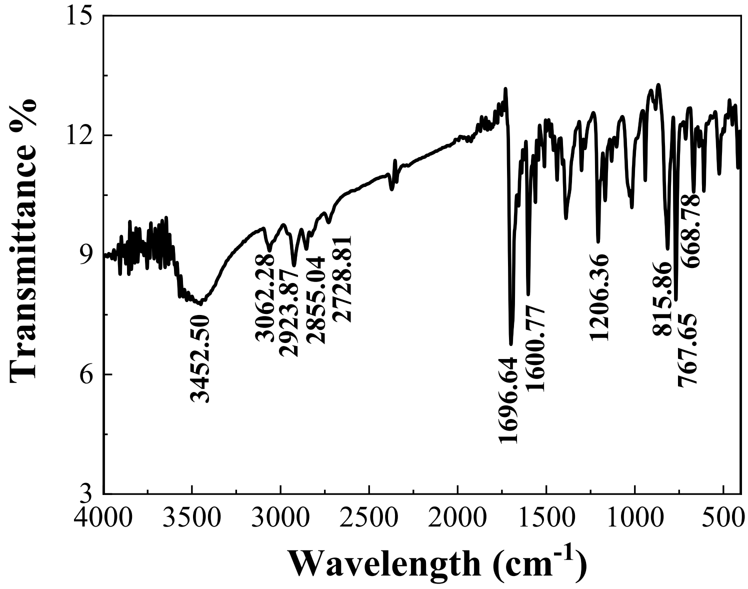


Fig. S10 IR spectrum of **HPFPA** (KBr).

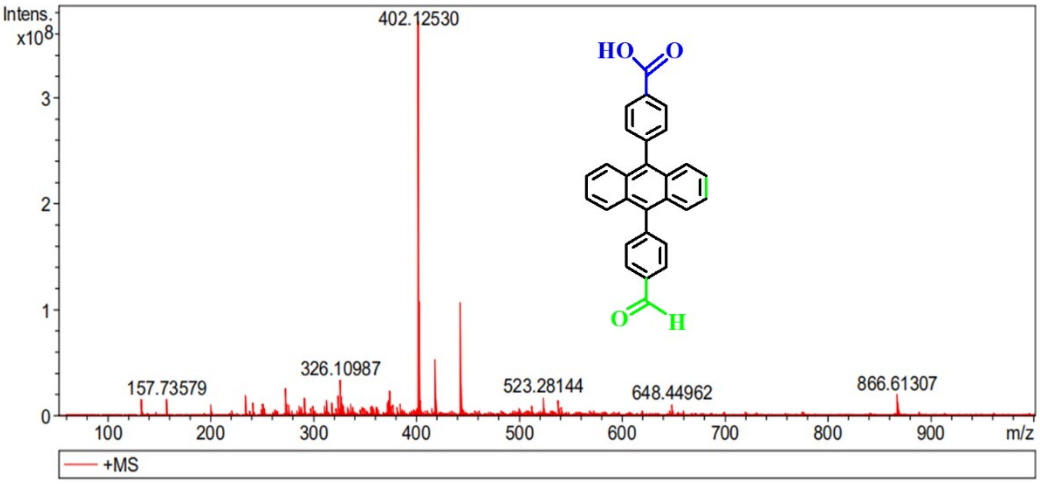


Fig. S11 Mass spectrum of **FPCPA** and molecular formula.

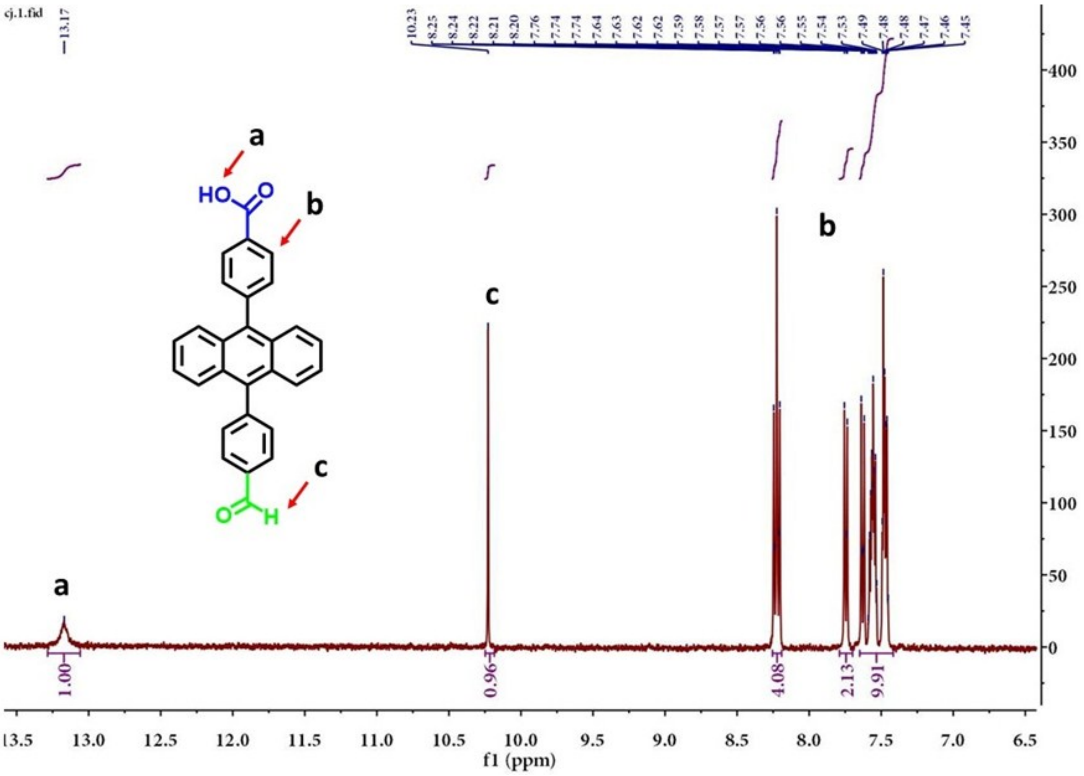


Fig. S12 ^{1}H NMR for **FPCPA** (solvent: DMSO-d$_6$)

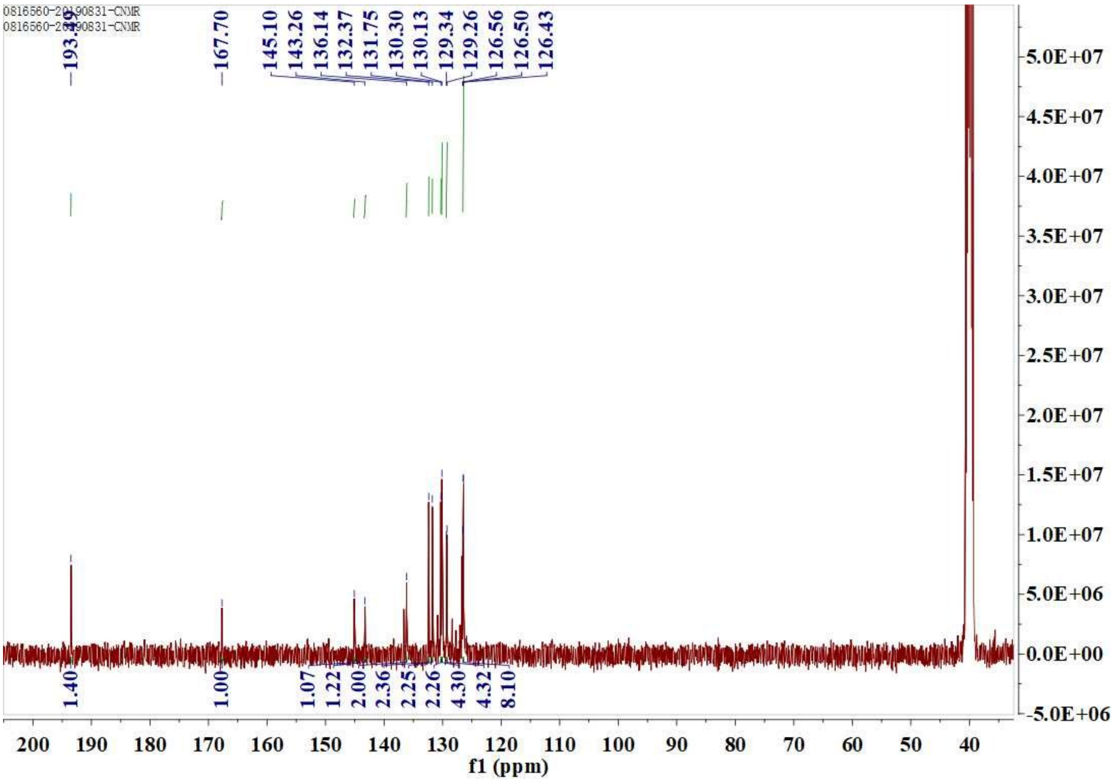


Fig. S13 ^{13}C NMR for **FPCPA** (solvent: DMSO-d_6)

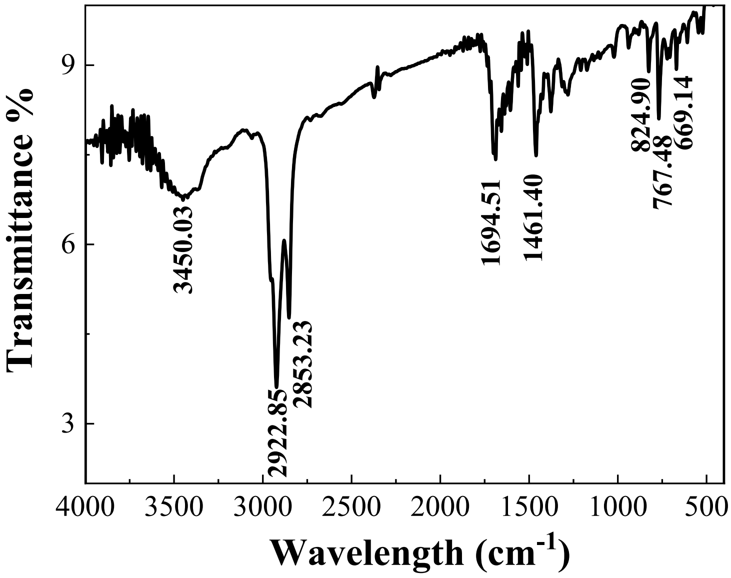


Fig. S14 IR spectrum of **FPCPA** (KBr).

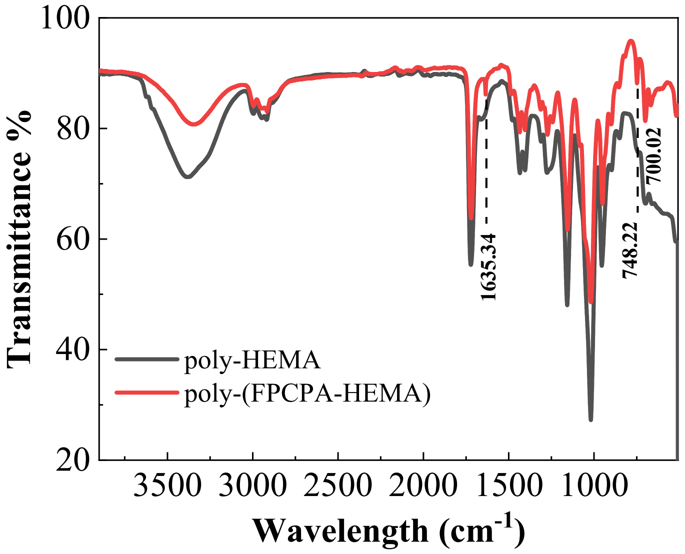


Fig. S15 IR spectra of poly-(FPCPA-HEMA) and poly-HEMA (ATR).

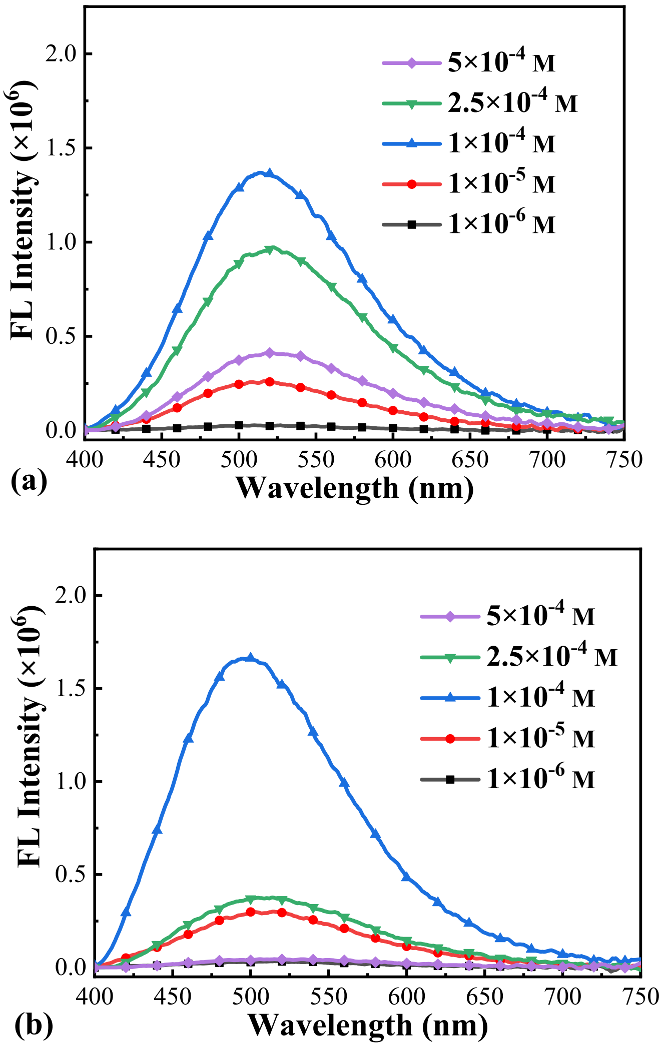


Fig. S16 Concentration-dependent fluorescence spectra of **HPFPA** (a) and **FPCPA** (b) in DMSO under the excitation of 398 nm.

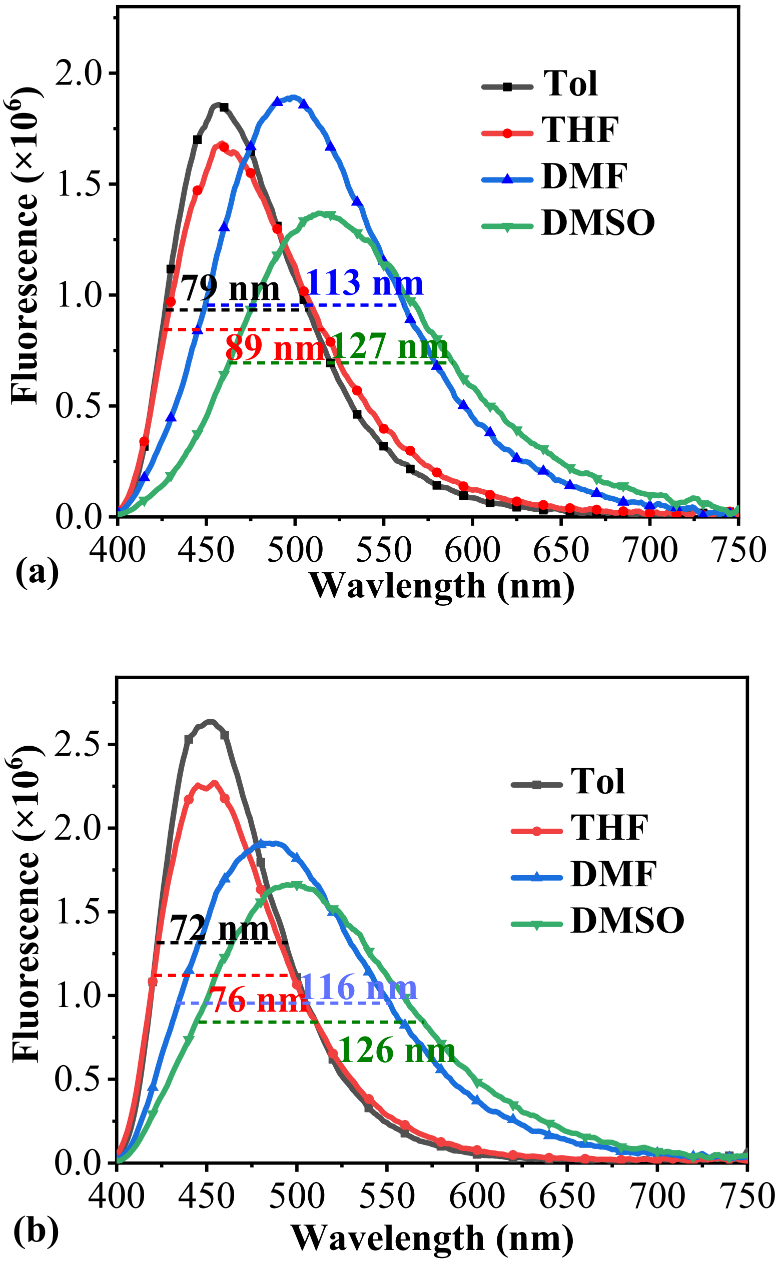


Fig. S17 Solvent-dependent fluorescence spectra of **HPFPA** (a) and **FPCPA** (b) under the excitation of 398 nm (1×10^{-4} M).

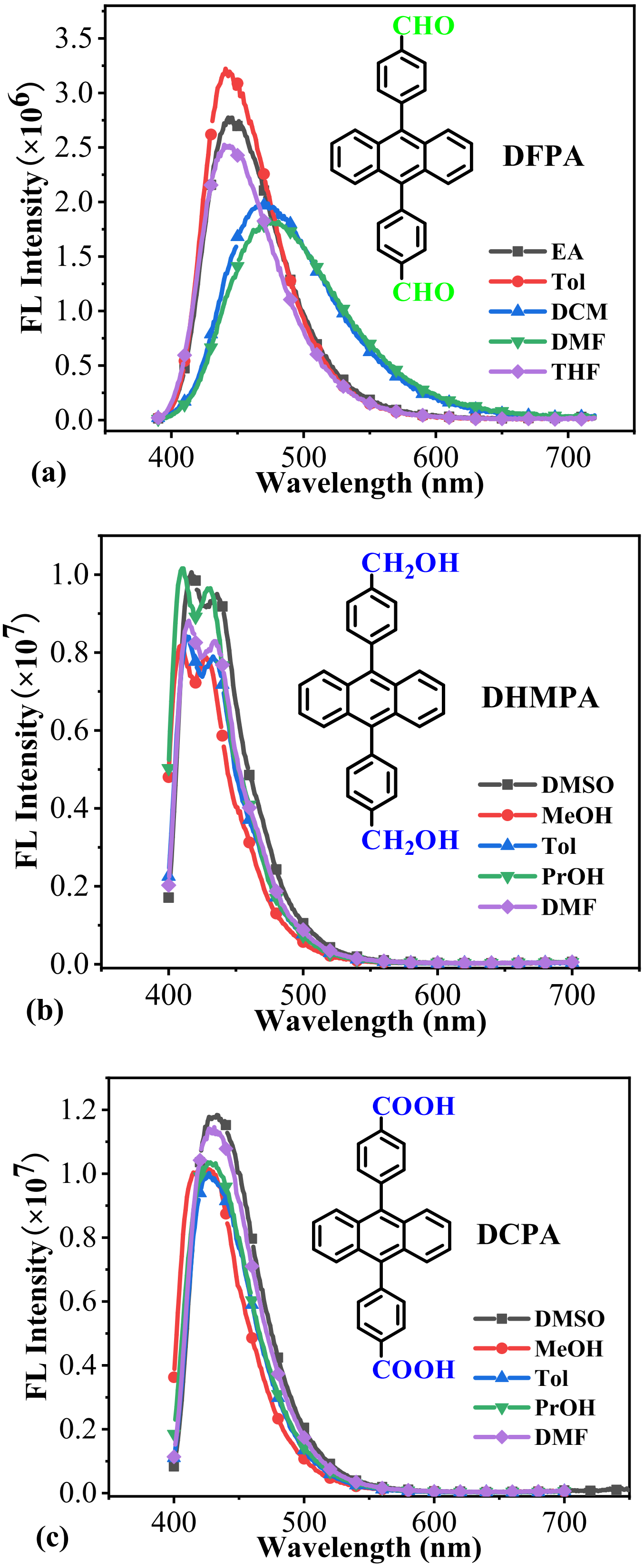
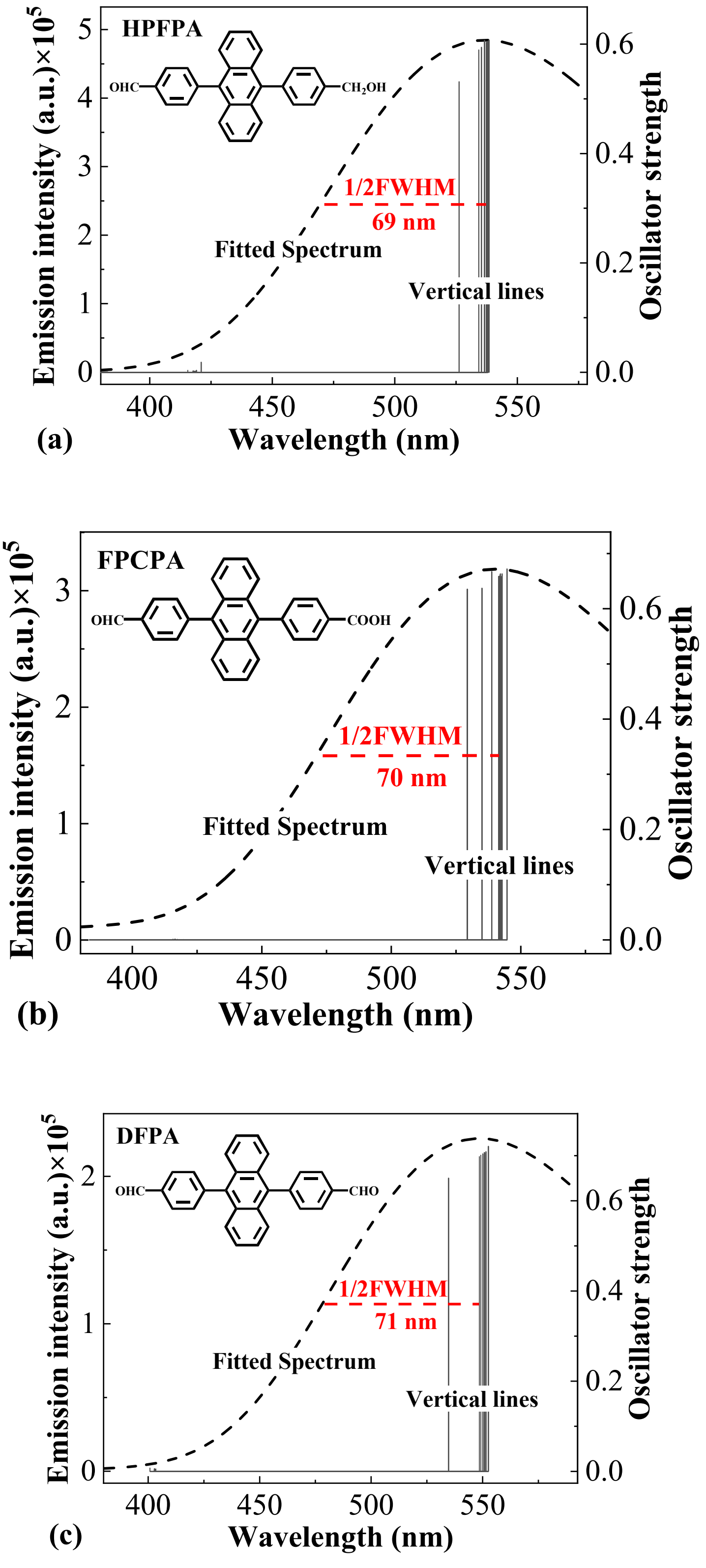
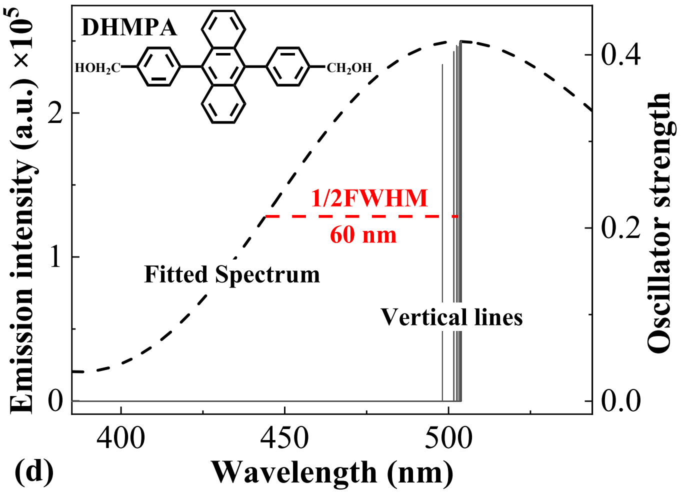
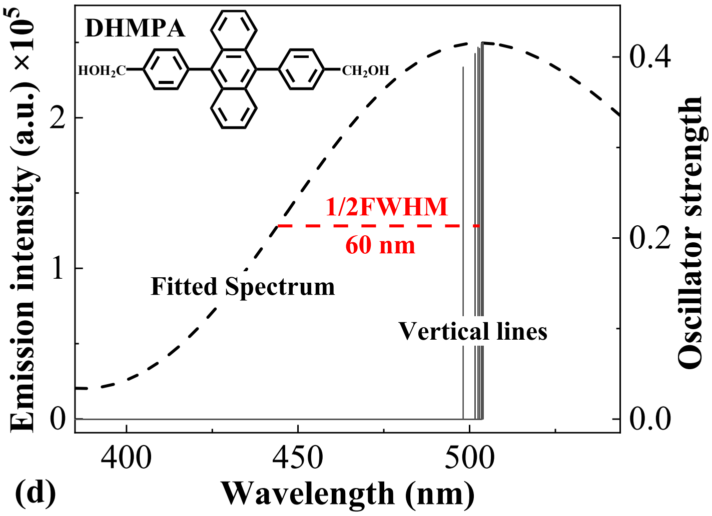


Fig. S18 Solvent-dependent fluorescence spectra of **DFPA** (a), **DHMPA** (b) and **DCPA** (c) under the excitation of the respective maximum absorption wavelength (2×10^{-5} M).


HPFPA
OHC
CH₂OH
1/2FWHM
69 nm
Fitted Spectrum
Vertical lines
Emission intensity (a.u.)×10⁵
0
1
2
3
4
5
Oscillator strength
0.0
0.2
0.4
0.6
400
450
500
550
Wavelength (nm)
(a)
FPCPA
OHC
COOH
1/2FWHM
70 nm
Fitted Spectrum
Vertical lines
Emission intensity (a.u.)×10⁵
0
1
2
3
Oscillator strength
0.0
0.2
0.4
0.6
400
450
500
550
Wavelength (nm)
(b)
DFPA
OHC
CHO
1/2FWHM
71 nm
Fitted Spectrum
Vertical lines
Emission intensity (a.u.)×10⁵
0
1
2
Oscillator strength
0.0
0.2
0.4
0.6
400
450
500
550
Wavelength (nm)
(c)



(d)



(d)

Fig. S19 The radiation transition probability, the radiation transition distribution and the correponding fitted fluorescence spectra for different chromophores.

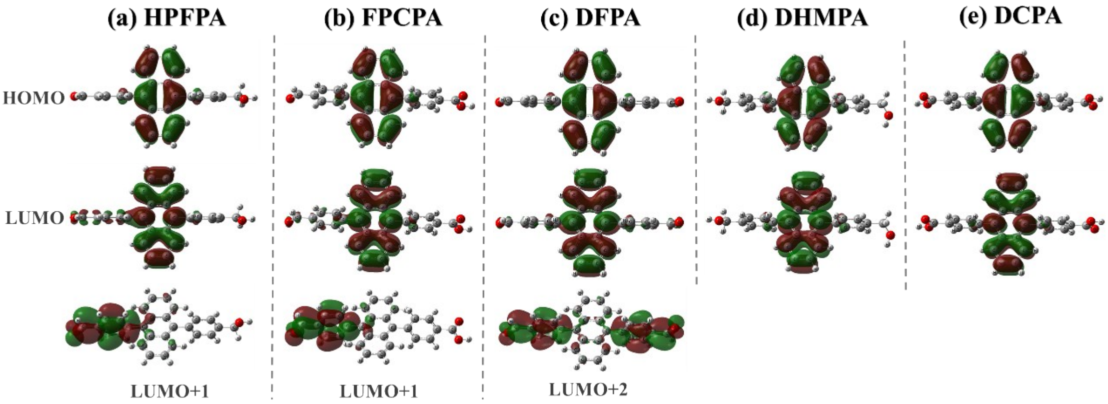


Fig. S20 The frontier molecular orbits for different chromophores obtained by employing PBE /6-311+G*.

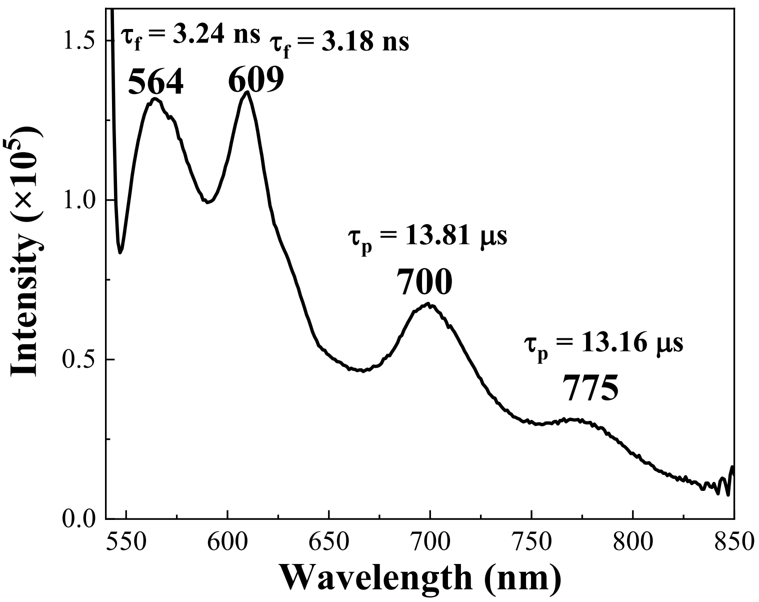


Fig. S21 Emission spectrum of PdBrTPP (4 μM) in DMSO (λ_{ex}=532 nm, r.t, in air).

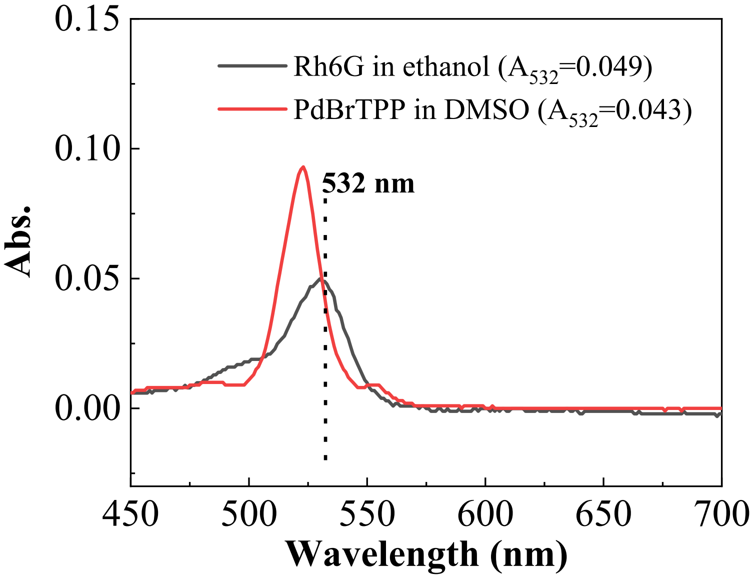


Fig. S22 Absorption spectra of PdBrTPP (4 μM) in DMSO and Rh6G (5×10^{-7} M) in ethanol. Here, Rh6G' concentration is at 5×10^{-7} M to ensure its absorbance (A_{532}) lower than 0.05 at the excitation wavelength of 532 nm.

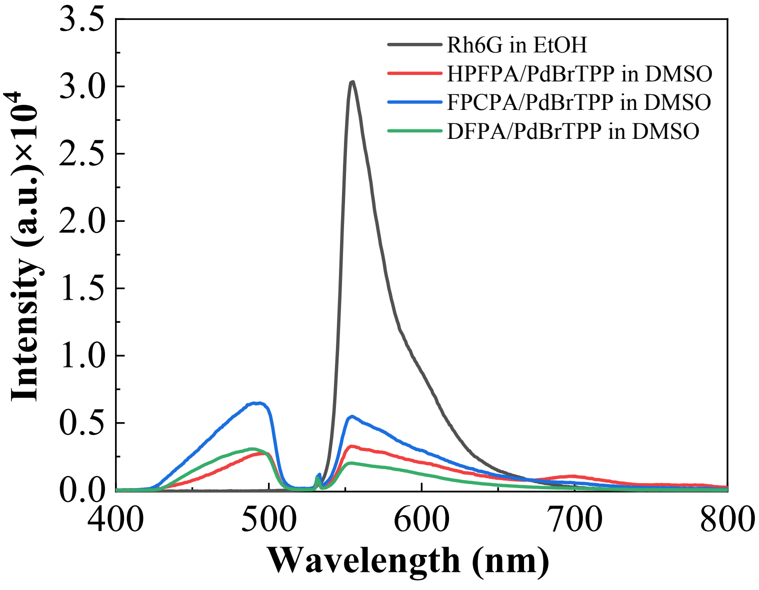


Fig. S23 Emission spectra of **HPFPA**/PdBrTPP, **FPCPA**/PdBrTPP and DFPA/PdBrTPP pairs in DMSO and of Rh6G (5×10^{-7} M) in ethanol (Curve for Rh6G is obtained by reducing the original measured data 15 times in the intensity scale). All spectra were obtained under the excitation of 532 nm diode laser using 532 nm filter ([annihilator]/[sensitizer]=1 mM/4 μM).

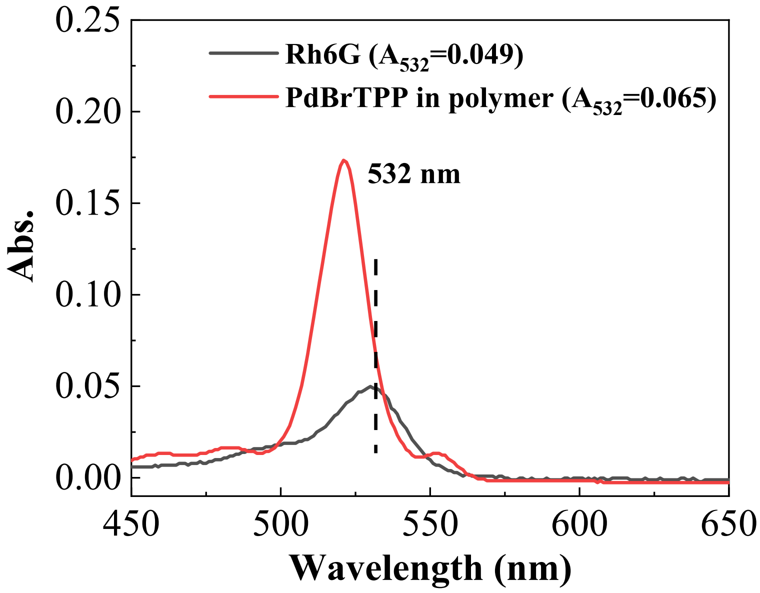


Fig. S24 Absorption spectrum of PdBrTPP (4 μM) in doped polymer measured in the 2-cm thick quartz colorimetric dish. The absorption spectrum of Rh6G in ethanol as the reference is also presented.

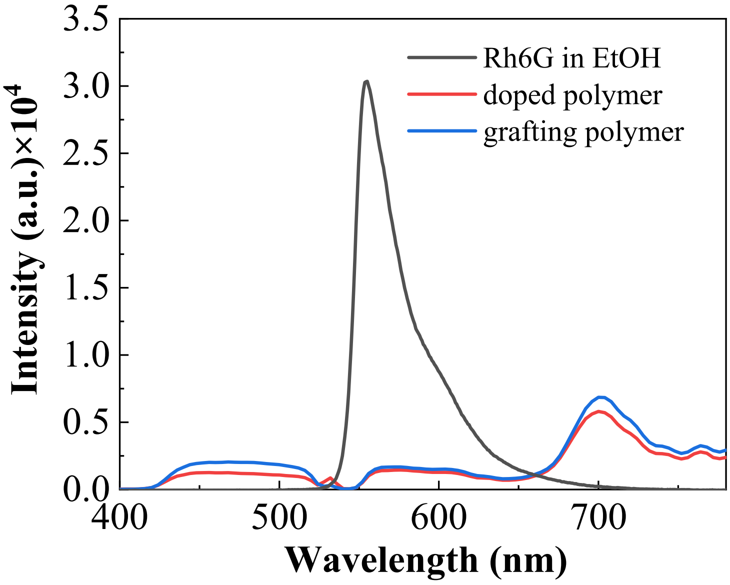


Fig. S25 Emission spectra of FPCPA/PdBrTPP ([FPCPA]/ [PdBrTPP]=1 mM/4 μM) in doped polymer and in grafting polymer measured in the 2-cm thick quartz colorimetric dish. The emission spectra of Rh6G in ethanol is also presented, which is obtained by reducing the original measured data 15 times in the intensity scale). All spectra were obtained by excited 532 nm diode laser using 532 nm filter.

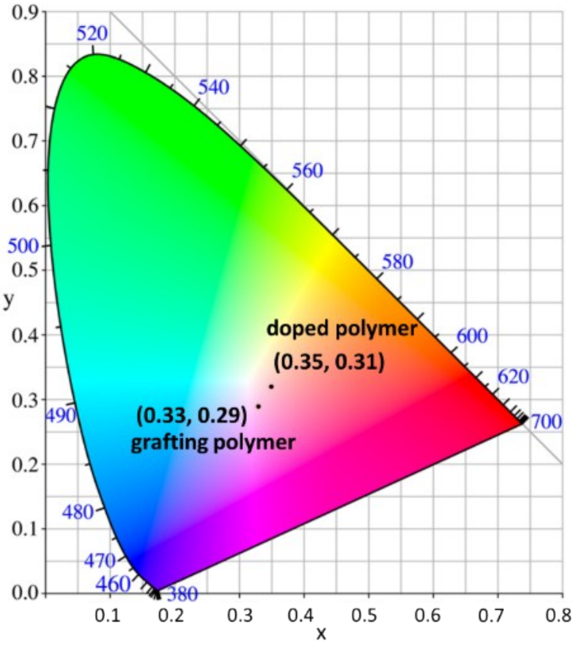


Fig. S26 The CIE diagrams of doped polymer and grafting polymer under the upconversion excitation with 532 filter.

Table S1 The optical properties including fluorescence quantum yields (Φ_f), lifetimes (τ_f), the radiative (k_f) and nonradiative decay rate constants (k_{nf}) of all chromophores in DMSO (1×10^{-5} M).

Compd.	λ_{abs} (nm)	λ_{fluo} (nm)	Φ_f	τ_f (ns)	k_f (10^8 s^{-1})	k_{nf} (10^8 s^{-1})
HPFPA	359, 378, 398	515	45.4%	4.56	1.00	1.20
FPCPA	359, 378, 398	498	56.5%	5.06	1.12	0.86
DFPA	359, 378, 398	459	23.9%	5.11	1.96	6.24
DHMPA	358, 378, 397	418, 435	91.8%	5.90	1.56	0.14
DCPA	358, 377, 397	432	96.2%	5.23	1.84	0.07

Table S2 The parameters based on the *Eqn.* (1) for different systems and reference Rh6G.

	$A_{532\text{ nm}}$	F	η	Φ_{WL} %
Rh6G	0.049	19390618	1.361	88.0
HPFPA/PdBrTPP in DMSO	0.043	430546	1.478	5.2
FPCPA/PdBrTPP in DMSO	0.043	721442	1.478	8.8
DFPA/PdBrTPP in DMSO	0.043	305456	1.478	3.7
FPCPA/PdBrTPP in doped polymer	0.065*	631078*	1.451	4.9
FPCPA/PdBrTPP in grafting polymer	0.065*	781445*	1.451	6.1

*These data are obtained from the polymer materials with 2-cm thick.