Electronic Supplementary Information

Constructing Diketopyrrolopyrrole-Based Fluorescent Porous Organic Polymer for Chromo Communication via Guest-to-Host Energy Transfer

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The supporting information contains the general experimental procedures, the synthesis and characterization details of the Br-DPP-m (Schemes S1) and 2-cyano-7-diethylamin coumarin molecules, the calculation of energy transfer efficiency Φ_{ET}, the thermogravimetric analysis of DPP-PPN-m (Fig. S1), the Fourier transform infrared spectroscopy of DPP-PPN-m (Fig. S2), the fluorescence spectra of monomers (Br-DPP-m) (Fig. S3), the pore size distribution of DPP-PPN-m (Fig. S4), the comparative analysis of data plots between fluorescence intensity and BET surface area for DPP-PPN-m (Fig. S5), the fluorescence decay profiles of DPP-PPN-m (Fig. S6), the nitrogen adsorption isotherms before and after loading of couramin (Fig. S7), the förster analysis of coumarin@DPP-PPN-3 illustrating the spectral overlap of DPP-PPN-3 acceptor and coumarin donor (Fig. S7).

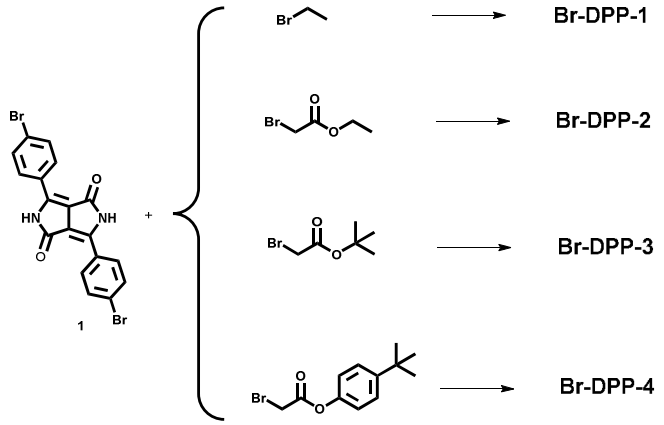
Materials

Commercial chemicals anddry solvents were used as received. 3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione[1] , tetrakis(4-ethynylphenyl)methane[2] , 2-cyano-7- diethylamin coumarin[3] were synthesized according to literature procedures.

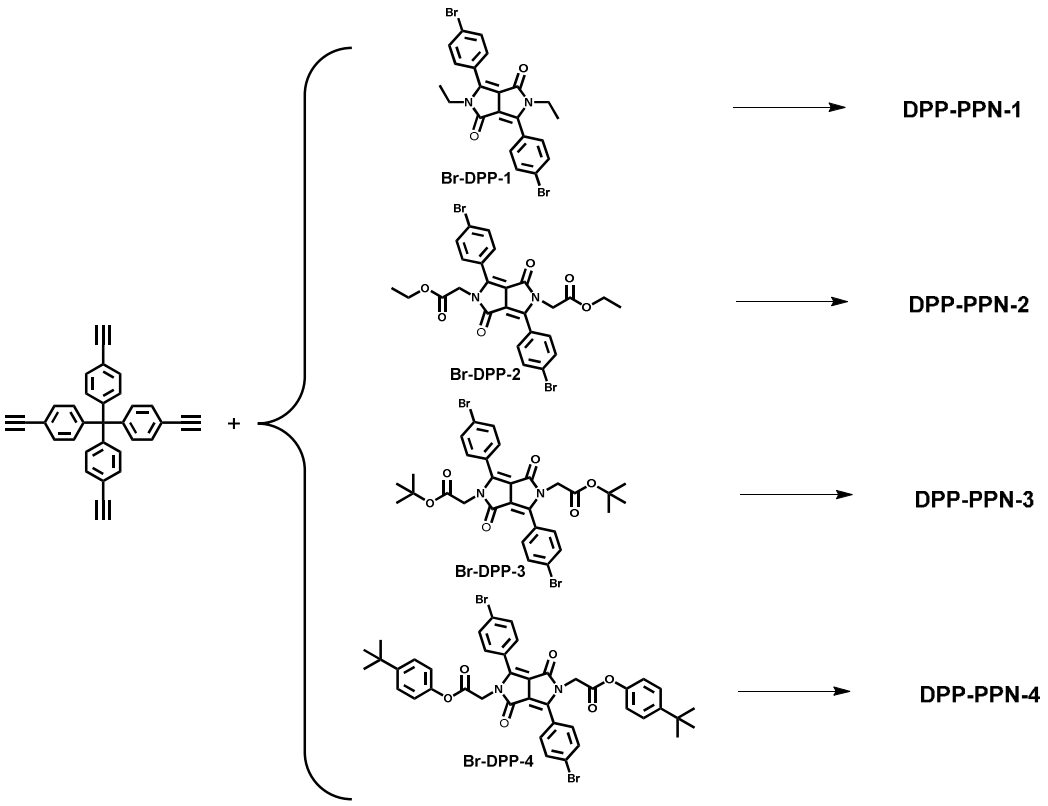
Synthesis of DPP-PPN-m

The synthetic route to the Br-DPP-m molecules is shown in Scheme S1; synthetic

route to the DPP-PPN-m is shown in Scheme S2.



Scheme S1 Synthesis of Br-DPP-m molecules

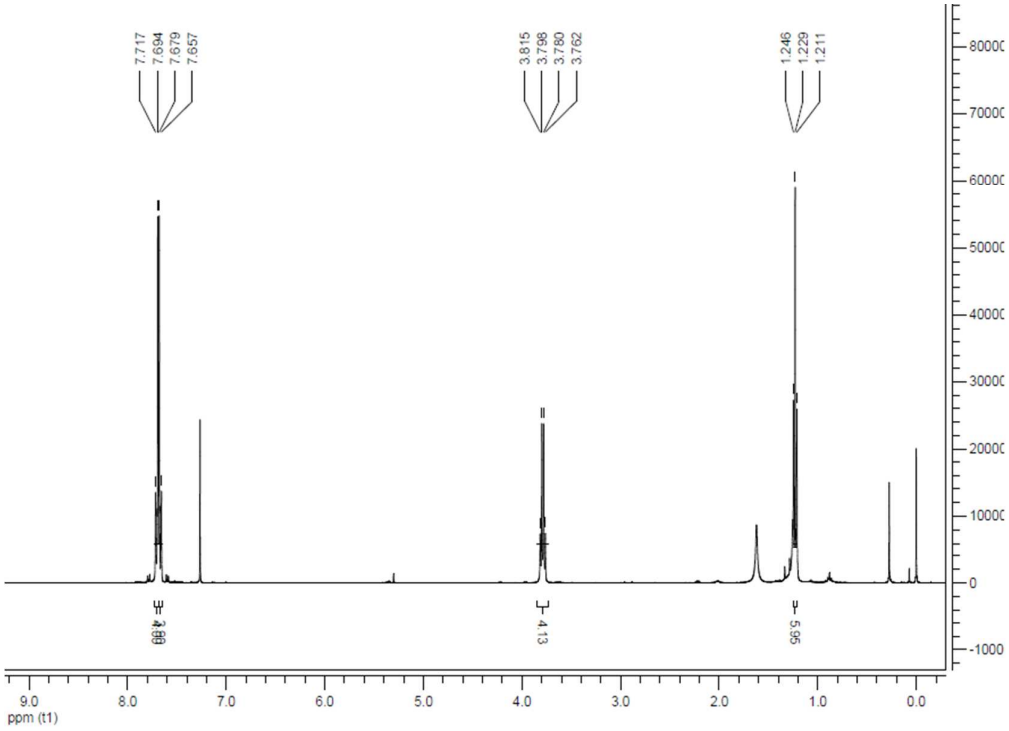


Scheme S2 Synthesis of DPP-PPN-m

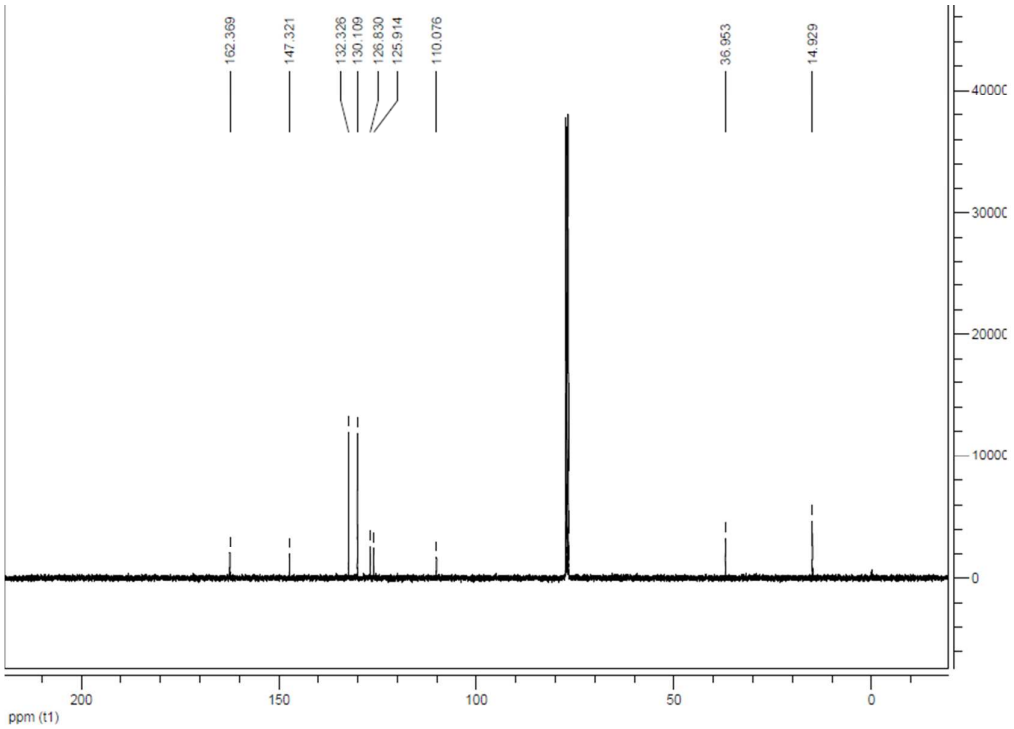
General procedure for Br-DPP-m

Compound **1** (0.223 g, 0.5 mmol), K_2CO_3 (0.276 g, 2 mmol)and 50 mL DMF were added into a three-necked flask, heated to 120°C for 30 min, alkylating agent (5 mmol) was added slowly. The mixture was kept at 120°C for 3 h. After cooled, 50 mL water was poured to quench the reaction, the mixture were filtered. The cake was dried under vacuum, then resolved in 50 mL CH_2Cl_2.The mixture was purified by column chromatography (silica gel) to give solid product.

Compound Br-DPP-1 : ^{1}HNMR(400MHz,$CDCl_3$): 1.23 (t, J = 7.2 Hz, 6H), 3.76-3.82 (m, 4H), 7.66-7.68 (m, 4H), 7.69-7.72 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9, 37.0, 110.1, 125.9, 126.8, 130.1, 132.3, 147.3, 162.4 ppm; HRMS (TOF-ESI$^+$): *m/z* calcd for $[C_{22}H_{18}Br_2N_2O_2Na]^+$: 522.9633; found: 522.9611.



^{1}HNMR (400MHz,$CDCl_3$) of Compound Br-DPP-1



^{13}C NMR (100 MHz, $CDCl_3$) of Compound Br-DPP-1

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
47 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-22 H: 0-19 N: 0-2 O: 0-2 Br: 0-2 Na: 0-1

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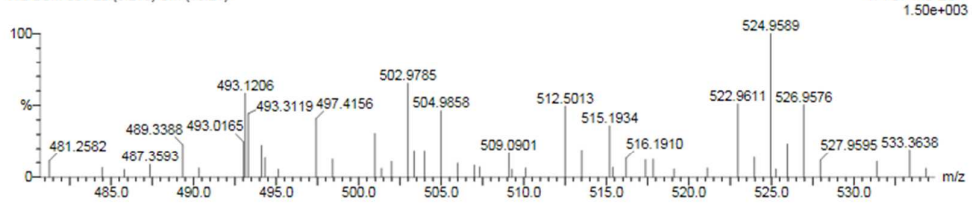
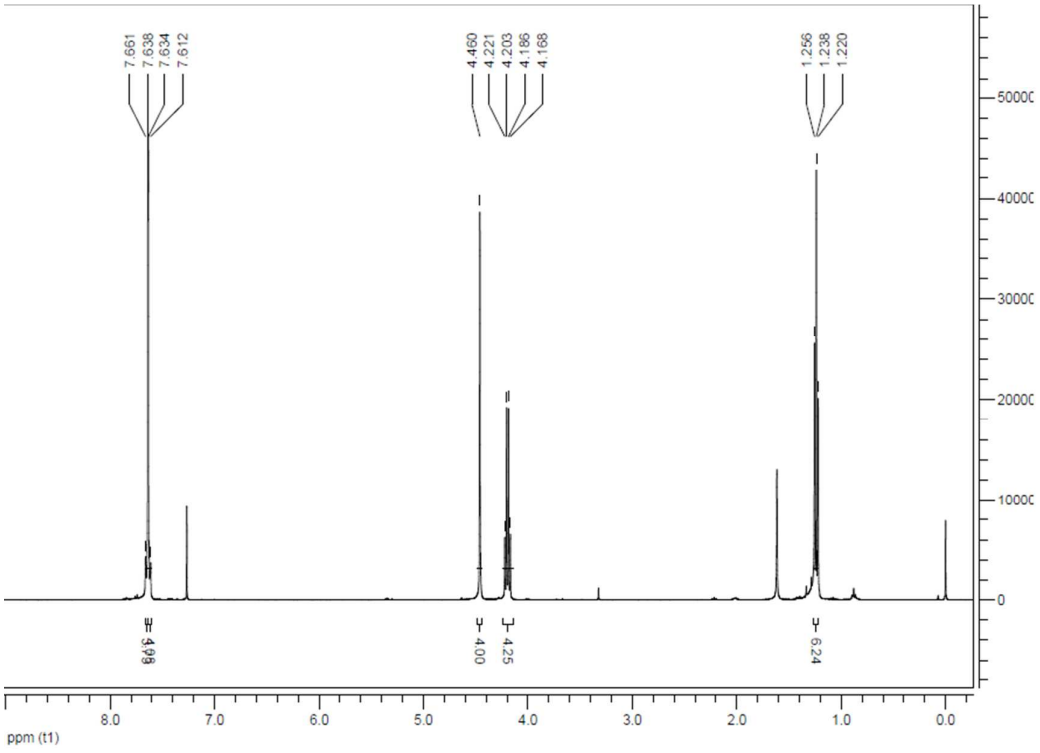


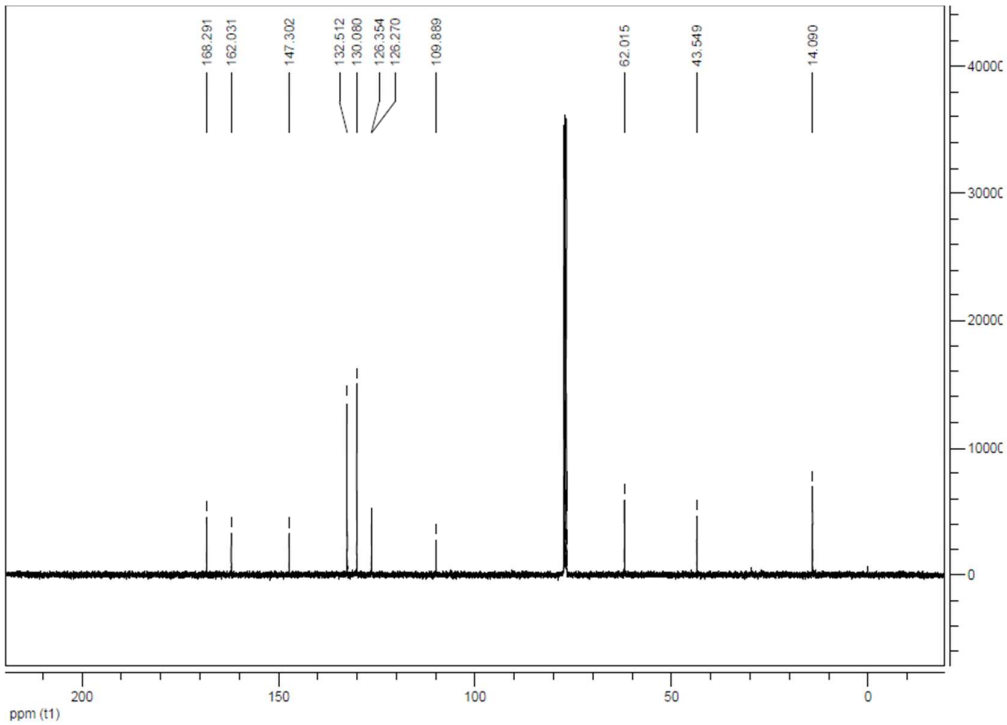
Minimum:		300.0	50.0	-1.5			
Maximum:				100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
522.9611	522.9633	-2.2	-4.2	13.5	14.5	0.0	C22 H18 N2 O2 Br2 Na

HRMS (TOF-ESI^+) of Compound Br-DPP-1

Compound Br-DPP-2 : ^{1}HNMR (400MHz,$CDCl_3$): 1.24 (t, J = 7.2 Hz, 6H), 4.17-4.22 (m, 4H), 4.46 (s, 4H), 7.61-7.66 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 43.5, 62.0, 109.9, 126.3, 126.4, 130.1, 132.5, 147.3, 162.0, 168.3 ppm; HRMS (TOF-ESI^{+}): *m/z* calcd for $[C_{26}H_{23}Br_2N_2O_2]^{+}$: 616.9923; found: 616.9940.



^{1}HNMR (400MHz,$CDCl_3$) of Compound Br-DPP-2



^{13}C NMR (100 MHz, $CDCl_3$) of Compound Br-DPP-2

Elemental Composition Report **Page 1**

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Number of isotope peaks used for i-FIT = 3

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85 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
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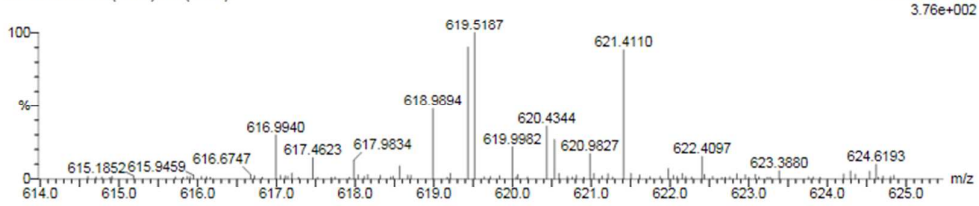
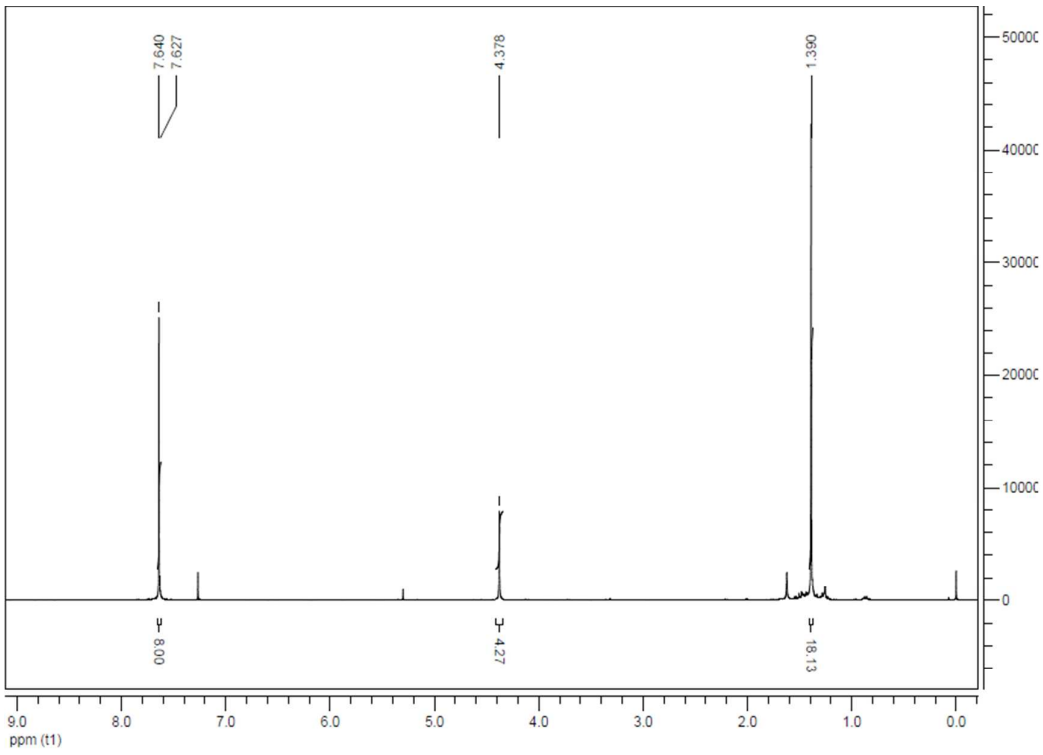


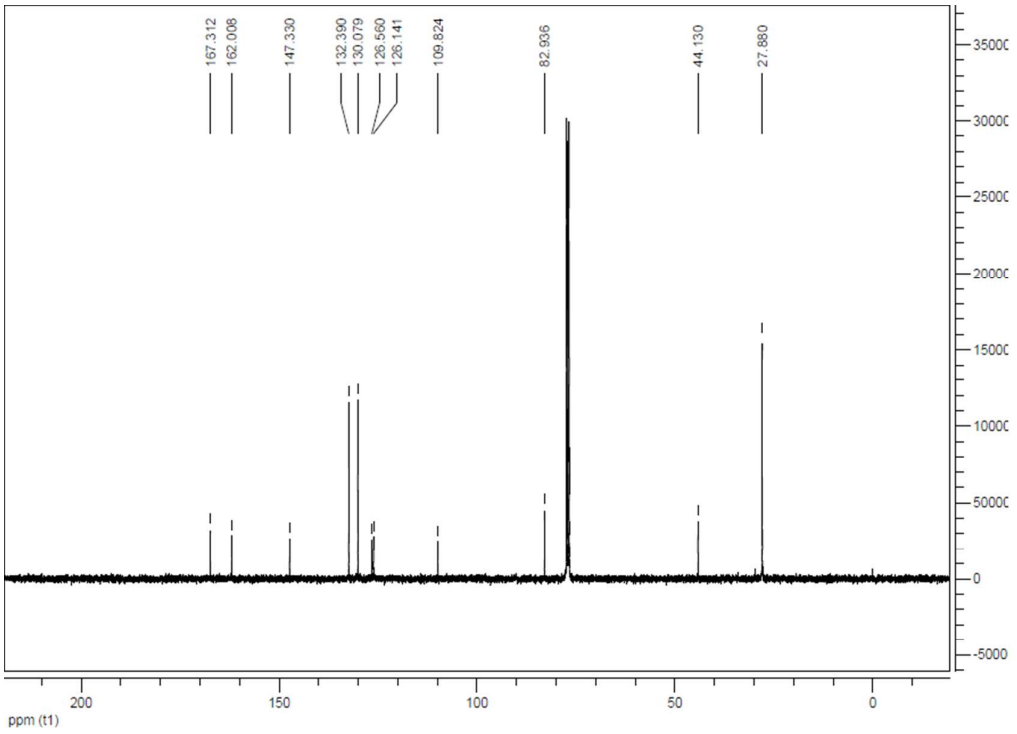
Minimum:				-1.5			
Maximum:		300.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
616.9940	616.9923	1.7	2.8	15.5	116.6	0.0	C26 H23 N2 O6 Br2

HRMS (TOF-ESI$^+$) of Compound Br-DPP-2

Compound Br-DPP-3 : ^{1}HNMR(400MHz,$CDCl_3$): 1.39 (s, 18H), 4.39 (s, 4H), 7.63-7.64 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.9, 44.1, 83.9, 109.8, 126.1, 126.6, 130.1, 132.4, 147.3, 162.0, 167.3 ppm; HRMS (TOF-ESI^{+}): *m/z* calcd for $[C_{30}H_{30}Br_2N_2O_2Na]^{+}$: 695.0368; found: 695.0373.



^{1}HNMR (400MHz,$CDCl_3$) of Compound Br-DPP-3



^{13}C NMR (100 MHz, $CDCl_3$) of Compound Br-DPP-3

Elemental Composition Report **Page 1**

Single Mass Analysis
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Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
118 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
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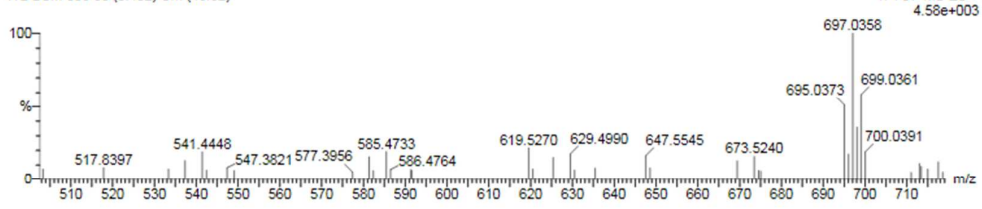
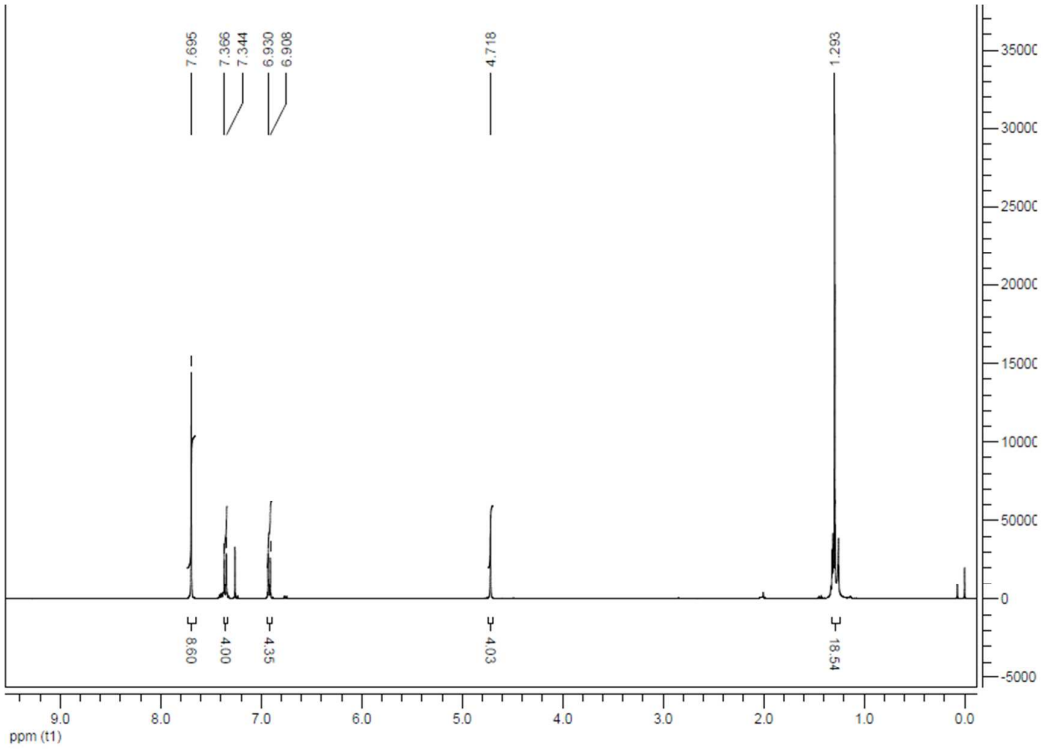


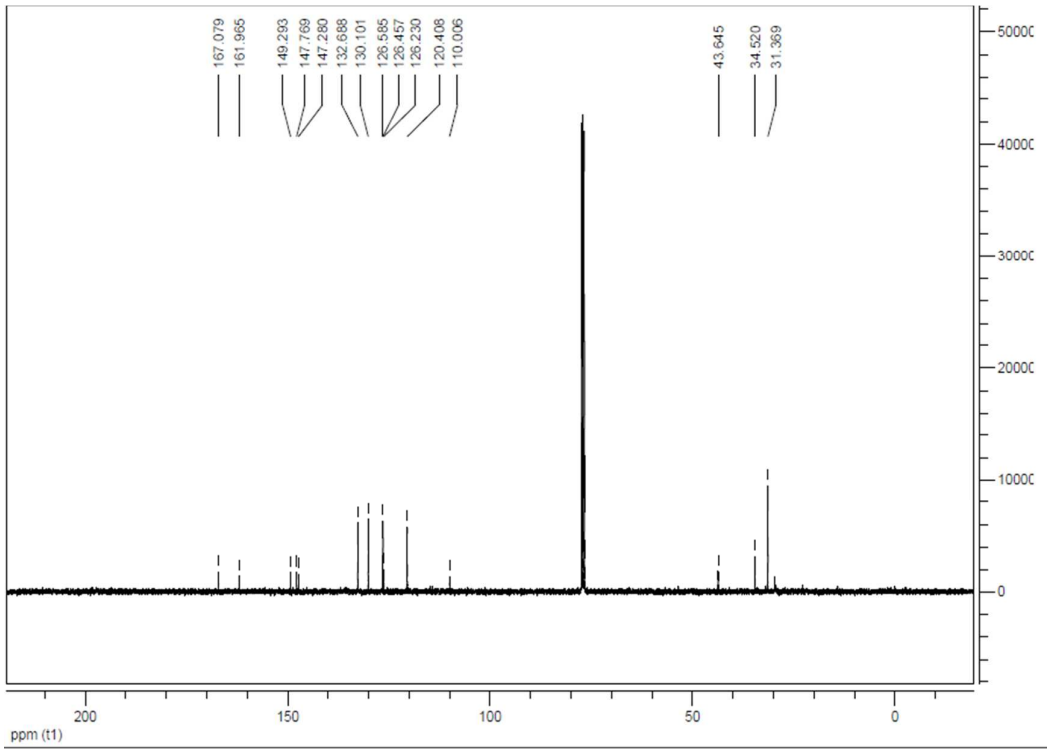
Minimum:				-1.5			
Maximum:		300.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
695.0373	695.0368	0.5	0.7	15.5	7.3	0.0	C30 H30 N2 O6 Na Br2

HRMS (TOF-ESI$^+$) of Compound Br-DPP-3

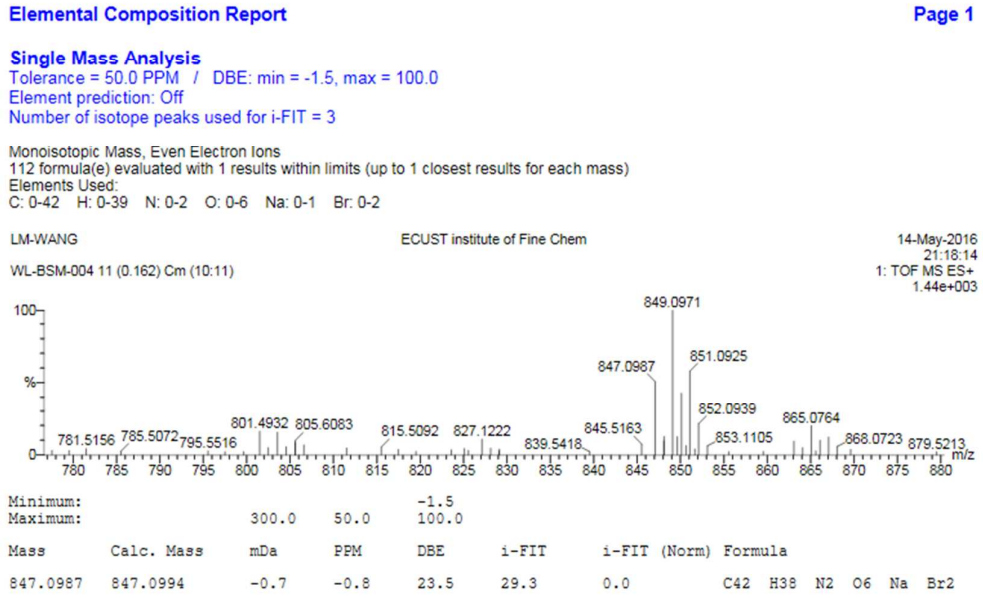
Compound Br-DPP-4 : ^{1}HNMR (400MHz,$CDCl_3$): 1.29 (s, 12H), 4.78 (s, 4H), 6.92 (d, J = 8.8 Hz, 4H), 7.36 (d, J = 8.8 Hz, 4H), 7.70 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.7, 34.5, 43.6, 110.0, 120.4, 126.2, 126.5, 126.6, 130.1, 132.7, 147.3, 147.8, 149.3, 162.0, 167.1 ppm; HRMS (TOF-ESI+): *m/z* calcd for $[C_{42}H_{38}Br_2N_2O_2Na]^+$: 847.0994; found: 847.0987.



^{1}HNMR (400MHz,$CDCl_3$) of Compound Br-DPP-4



^{13}C NMR (100 MHz, $CDCl_3$) of Compound Br-DPP-4



HRMS (TOF-ESI+) of Compound Br-DPP-4

General procedure for DPP-PPN-m

tetrakis(4-ethynylphenyl)methane (1 equiv, 50 mg, 0.12 mmol) and the appropriate Br-DPP-m (2 equiv, 0.24 mmol) in toluene/ triethylamine (1:1 v/v 3 mL) at 80 ^{o}C using Palladium(0)tetrakis(triphenylphosphine) (0.14 mol%, 20 mg) and copper(I) iodide (0.26 mol%, 6 mg) as catalysis for 3d. After cooling to room temperature the precipitated polymers was isolated by filtration over a Büchner funnel and washed with 1 M hydrochloric acid (20 mL), followed with excess methanol, tetrahydrofuran and dichloromethane. Then the product was further extracted with dichloromethane by Soxhlet apparatus for 24 h. The solvent was removed under vacuum at room temperature to afford the DPP-PPN-m. Anal. Calcd. for DPP-PPN-1: C, 83.96; H, 5.08; N, 5.08. Found: C, 82.79; H, 4.56; N, 4.01; Anal. Calcd. for DPP-PPN-2: C, 77.27; H, 4.80; N, 4.20. Found: C, 76.86; H, 4.46; N, 3.81;Anal. Calcd. for DPP-PPN-3:C, 77.25; H, 5.54; N, 3.88. Found: C, 73.20; H, 5.04; N, 3.28; Anal. Calcd. for DPP-PPN-4: C, 80.23; H, 5.49; N, 3.20. Found: C, 79.45; H, 4.67; N, 3.01.

Calculation of energy transfer efficiency Φ_{ET}[4]

Φ_{ET} value was calculated by the following equation:

$$\Phi_{ET} = k_e/(k_o + k_e) \quad \text{, eq. S1}$$

Where k_e refers to the energy transfer constant and K_o represents the sum of radiative and non-radiative constants. k_e and K_o value were calculated from lifetime of donor molecule τ_0 and donor molecule in the presence of acceptor $\tau_{D\text{-}A}$. $\tau_0=1/ k_o$ and $\tau_{D\text{-}A}=1/(k_o+ k_e)$.

Calculation of spectral overlap integral (J) and Förster critical radius (R_0)[5]

Spectral overlap integral (J) value was calculated by the following equation:

$$J = \int F(\lambda)\varepsilon(\lambda)\lambda^4 d\lambda \quad \text{, eq. S2}$$

Where F(λ) is the fluorescence spectrum of the donor normalized so that $\int_0^\infty F(\lambda)d\lambda = 1$. Refers to the molar extinction sprectrum of the acceptor. For R_0 in Å, λ in nm, J in M^{-1} cm^{-1} nm^4, we can obtain:

$$R_0 = 0.2108(\kappa^2 \Phi_D n^{-4} J)^{1/6}, \text{ eq. S3}$$

Where κ^2 is orientational factor, Φ_D is fluorescence quantum yield of the donor and n is the refractive index of the medium. In this work, κ^2 and Φ_D are assumed to be equal to 2/3 and 0.1, respectively.

Table S1 element analysis of DPP-PPNs

	Calculated			Found		
	C%	H%	N%	C%	H%	N%
DPP-PPN-1	83.96	5.08	5.08	82.79	4.56	4.01

DPP-PPN-2	77.27	4.80	4.20	76.86	4.46	3.81
DPP-PPN-3	77.25	5.54	3.88	73.20	5.04	3.28
DPP-PPN-4	80.23	5.49	3.20	79.45	4.67	3.01

Table S2 ET efficiency, overlap integral and foster radius of reported energy transfer system

ET systems	ET efficiency (%)	Overlap integral ($M^{-1}cm^{-1}nm^4$)	Foster radius (R_0) (nm)	Reference
DPB-BI-1	65	$6.25*10^{-14}$ $M^{-1}cm^3$	23	4
DPB-BI-1	53	$6.25*10^{-14}$ $M^{-1}cm^3$	23	
BI@2	72	$4.57*10^{-14}$ $M^{-1}cm^3$	21	
PP-CMP⊃couma rin 6	91			6
Zn_2(ZnTCPP) based MOF (1)	15	$4.1*10^{-14}$ cm^{-6}	3	7
TPE-NCMP-4/NR	90			8
QTH+NR	56.6	$1.17*10^{15}$ $M^{-1}cm^{-1}nm^4$	32.3	9
CS-PS clay hybrids (state-A)	50			10
CS-PS clay hybrids (state-B)	10			
Rh6G in Au-MCM-41 solution	51.8			11

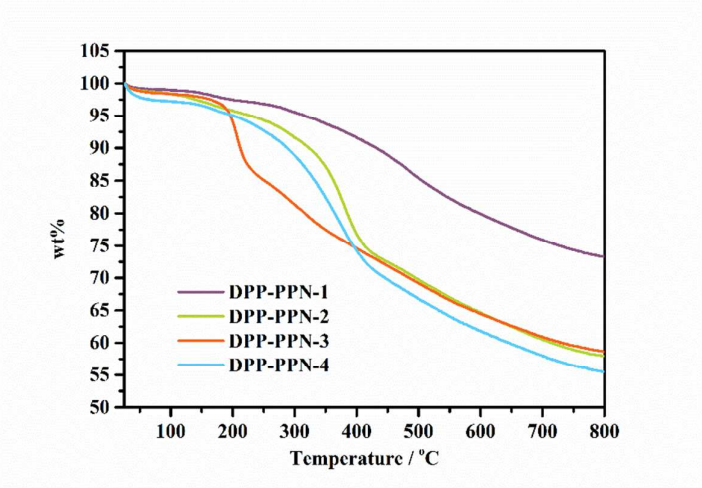


Fig. S1 Thermogravimetric analysis of DPP-PPN-m

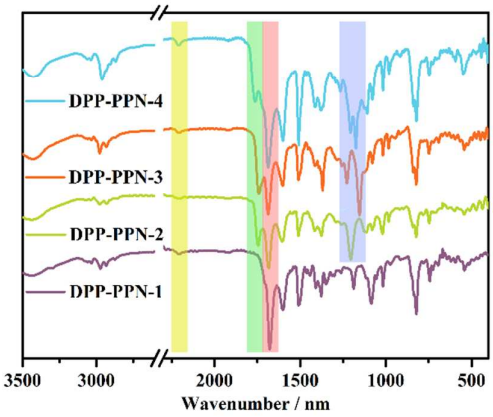


Fig. S2 Fourier transform infrared spectroscopy of DPP-PPN-m

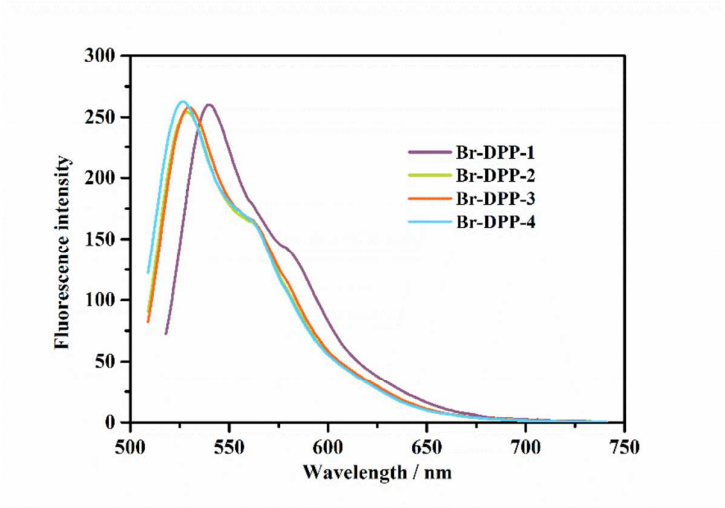


Fig. S3 Fluorescence spectra of monomers (Br-DPP-m)

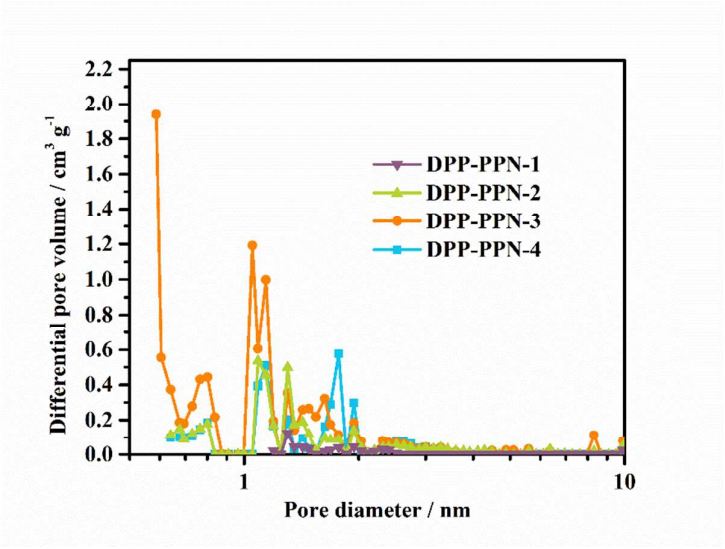


Fig.S4 Pore size distribution of DPP-PPN-m

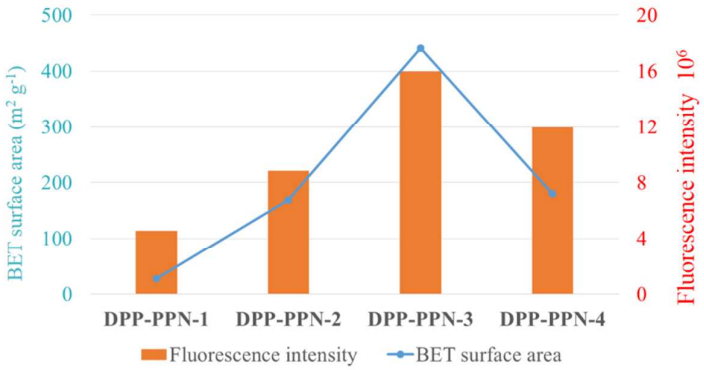


Fig. S5 Comparative analysis of data plots between fluorescence intensity and BET surface area for DPP-PPN-m.

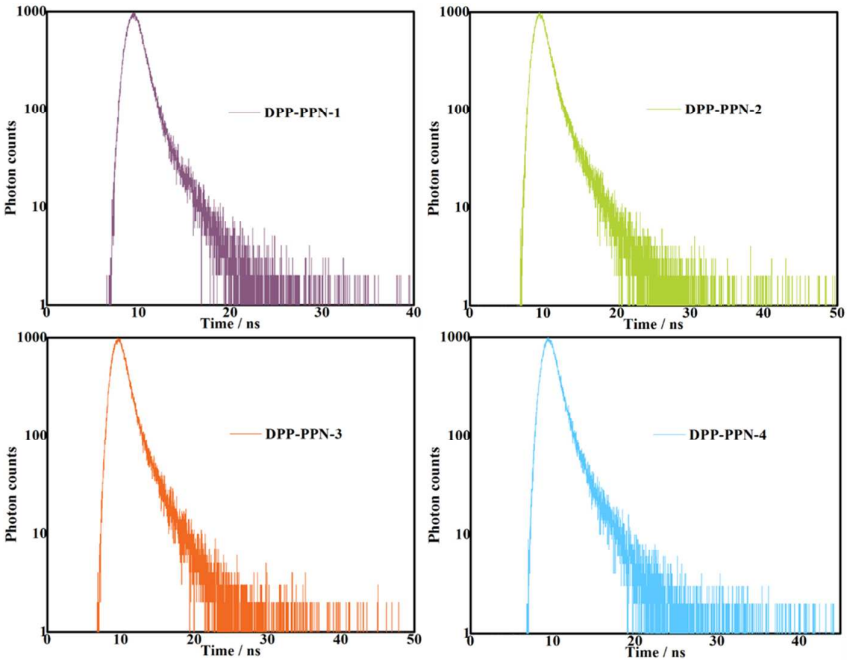


Fig. S6 Fluorescence decay profiles of DPP-PPN-m

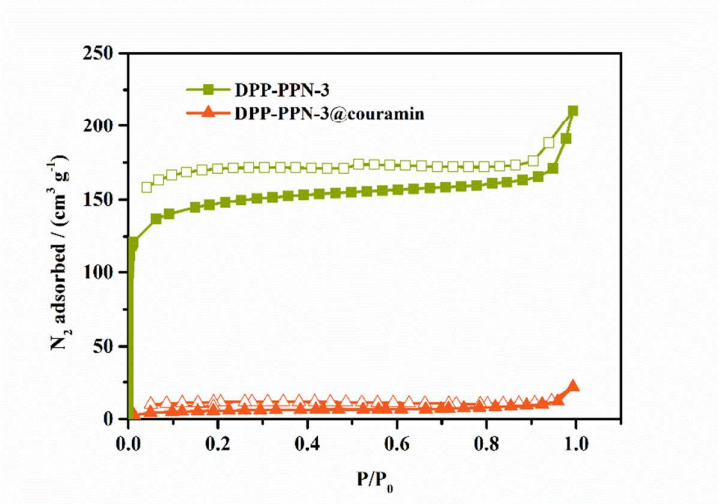


Fig.S7 Nitrogen adsorption isotherms before and after loading of couramin.

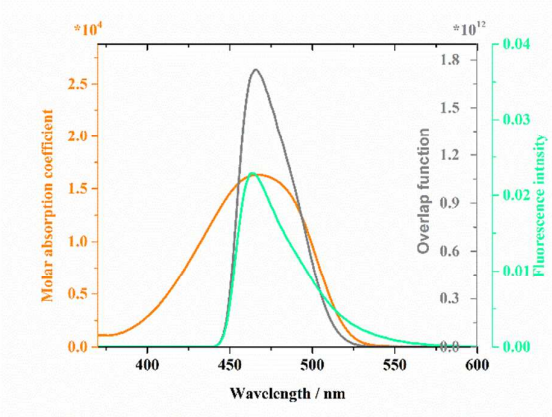


Fig. S8 Förster analysis of coumarin@DPP-PPN-3 illustrating the spectral overlap of DPP-PPN-3 acceptor and coumarin donor. green line: fluorescence spectrum of coumarin (donor); orange line: molar extinction spectrum of Br-DPP-3 (acceptor); grey line: overlap function $f(\lambda) = F(\lambda)\varepsilon(\lambda)\,\lambda^4$. The spectral overlap integral (J) value was calculated to be 6.68×10^{14} M^{-1} cm^{-1} nm^4. The estimated R_0 value was calculated to be 31 Å according to eq. S3.

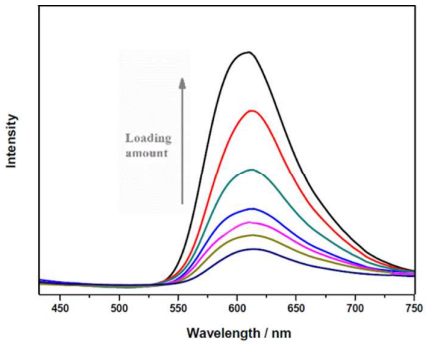


Fig. S9 Fluorescence spectral change of coumarin@DPP-PPN-3 with different coumarin contents (0-23.4 mol%) upon excitation at 390 nm.

References

1 Qu, Y.; Hua, J.; Tian, H., Colorimetric and ratiometric red fluorescent chemosensorfor fluoride ion based on diketopyrrolopyrrole. *Org. Lett.*, **2010,** *12*, 3320-3323.

2 Pandey, P.; Farha, O. K.; Spokoyny, A. M.; Mirkin, C. A.; Kanatzidis, M. G.; Hupp, J. T.; Nguyen, S. T., A "click-based" porous organic polymer from tetrahedral building blocks. *J. Mater Chem.,* **2011,** *21*, 1700-1703.

3 Wu, M.; He, T.; Li, K.; Wu, M.; Huang, Z.; Yu, X., A real-time colorimetric and ratiometric fluorescent probe for sulfite. *Analyst,* **2013,** *138*, 3018-3025.

4 Dolgopolova, E. A.; Williams, D. E.; Greytak, A. B.; Rice, A. M.; Smith, M. D.; Krause, J. A.; Shustova, N. B., A Bio-inspired Approach for Chromophore Communication: Ligand-to-Ligand and Host-to-Guest Energy Transfer in Hybrid Crystalline Scaffolds. *Angew. Chem. Int. Ed*. **2015,** *54*, 13639-13643.

5 B. Valeur, in *Molecular Fluorescence*, Wiley-VCH Verlag GmbH, **2001,** DOI: 10.1002/3527600248.ch4, pp. 72.

6 Chen L, Honsho Y, Seki S, Jiang D. Light-harvesting conjugated microporous polymers: rapid and highly efficient flow of light energy with a porous polyphenylene framework as antenna. *J. Am. Chem. Soc.* **2010**, *132*, 6742-6748.

7 Williams DE, Rietman JA, Maier JM, et al. Energy Transfer on Demand: Photoswitch-Directed Behavior of Metal–Porphyrin Frameworks. *J. Am. Chem. Soc.* **2014**, *136*, 11886-11889.

8 Zhang, P.; Wu, K.; Guo, J.; Wang, C., From hyperbranched polymer to nanoscale CMP (NCMP): improved microscopic porosity, enhanced light harvesting, and enabled solution processing into white-emitting Dye@ NCMP films. *ACS Macro Lett.*, **2014,** *3*, 1139-1144.

9 Bhattacharyya, S.; Jana, B.; Patra, A., Multichromophoric organic molecules encapsulated in polymer nanoparticles for artificial light harvesting. *ChemPhysChem,* **2015,** *16*, 796-804.

10 Rao, K. V.; Datta, K. K. R.; Eswaramoorthy, M.; George, S. J., Light−Harvesting Hybrid Hydrogels: Energy−Transfer−Induced Amplified Fluorescence in Noncovalently Assembled Chromophore–Organoclay Composites. *Angew. Chem. Int. Ed.*, **2011,** *123*, 1211-1216.

11 Sen, T.; Jana, S.; Koner, S.; Patra, A., Energy transfer between confined dye and surface attached Au nanoparticles of mesoporous silica. *J. Phys. Chem. C.*, **2009,** *114*, 707-714.