V-shaped chiral hosts based on π-extended hematoxylin

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Supporting Information

1. Materials

Hematoxylin (HX), 3, 4, 5, 6-Tetrafluorophthalonitirle, Tetrafluoroterephthalonitirle, 1,2-Difluoro-4, 5-dinitrobenzene, C_{60}, N,N-dimethylformamide, potassium carbonate, ethyl acetate, sodium sulfate and other chemical reagents were all commercially available from Sinopharm Chemical Reagent Co. Ltd., China.

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2. Synthesis

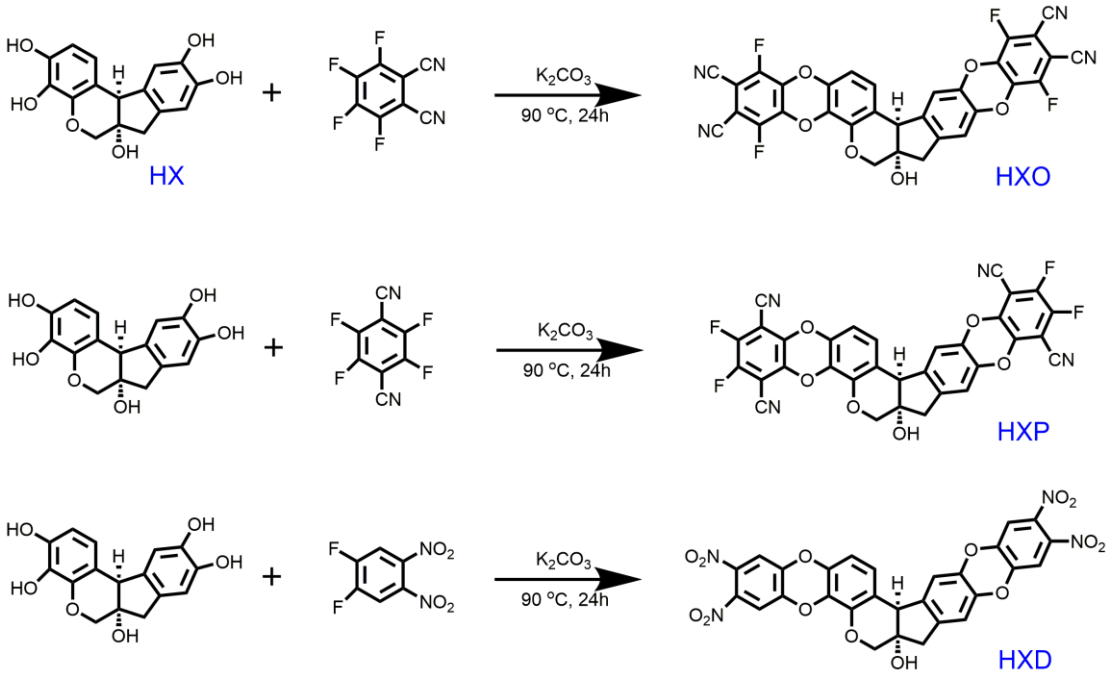


Fig. S1 Synthesis route of HXO, HXP and HXD.

HXO, HXP and HXD were synthesized as below. In detail, 2 mmol HX and 5 mmol 3, 4, 5, 6-Tetrafluorophthalonitirle (or Tetrafluoroterephthalonitirle, or 1,2-Difluoro-4, 5-dinitrobenzene) were dispersed in 30 mL DMF, afterwards potassium carbonate (12 mmol) was added as the catalysis. The mixture was stirred under nitrogen protection at 90 ^{o}C for 24 hours and then cooled to room temperature. The obtained solution was acidified with 1N HCl to adjust the pH to about 4 and extracted with ethyl acetate. The organic layer was washed with deionized water, dried with Na_2SO_4 and filtered. The filtrate was evaporated and the crude product was purified by the short pad of silica gel column chromatography (dichloromethane and petroleum ether) to obtain the product (HXO, HXP and HXD).

HXO: ^{1}H NMR (400 MHz, d6-DMSO) δ 7.35 (m, 1H), 7.14 (m, 2H), 6.81 (m, 1H), 4.06 (t, J = 16 Hz, 2H), 3.83 (d, J = 8 Hz, 1H), 2.97 (m, 2H). ^{13}C NMR (100 MHz, d6-DMSO) δ 30.16, 36.36, 41.81, 50.30, 70.18, 76.44, 109.19, 110.82, 111.51, 113.70, 114.38,122.19, 126.83, 128.46, 138.59, 142.15, 144.08, 162.71. ^{19}F NMR (376 MHz, d6-DMSO) δ -130.03 (m, 2F), -131.84 (m, 2F). MS (ESI) calcd. for $C_{32}H_{11}F_4N_4O_6$ [MH^+], m/z = 623.4551, found m/z = 623.5000. (yield 43.76%)

HXP: ^{1}H NMR (400 MHz, d6-DMSO) δ 7.38 (d, J = 8 Hz, 1H), 7.15 (m, 2H), 6.82 (d, J = 8 Hz, 1H),

5.71 (s, 1H), 4.07 (d, J = 8 Hz, 2H), 3.86 (d, J = 12 Hz, 1H), 2.98 (s, 2H). ^{13}C NMR (100 MHz, d6-DMSO) δ 31.25, 36.11, 41.75, 50.21, 55.46, 70.13, 76.37, 95.85, 109.00, 113.73, 114.29, 122.01, 126.87, 128.52, 138.20, 138.63, 141.67, 142.10, 162.84. ^{19}F NMR (376 MHz, d6-DMSO) δ -137.78 (m, 2F), -137.95 (s, 2F). MS (ESI) calcd. for $C_{32}H_{11}F_4N_4O_6$ [MH^+], m/z = 623.4551, found m/z = 623.4967. (yield 53.56%)

HXD: ^{1}H NMR (400 MHz, d6-DMSO) δ 10.98 (s, 2H), 7.53 (m, 2H), 7.14 (t, 1H), 6.92 (m, 2H), 6.68 (m, 3H), 5.64 (s, 1H), 4.01 (m, 2H), 3.75 (d, J = 12 Hz, 1H), 2.93 (m, 2H). ^{13}C NMR (100 MHz, d6-DMSO) δ 29.42, 41.92, 49.88, 69.93, 76.46, 106.15, 108.60, 112.65, 113.05, 113.83, 129.06, 129.84, 131.14, 133.88, 139.60, 142.33, 147.68, 151.20. MS (ESI) calcd. for $C_{28}H_{15}N_4O_{14}$ [MH^+], m/z = 631.4415, found m/z = 631.3454. (yield 37.25%)

3. Analytical instruments and methods

^{1}H NMR, ^{13}C NMR spectra and ^{19}F NMR were obtained by BRUKER AVANCE III HD 400 at room temperature. High-Resolution Mass Spectra (HR-MS) was carried on an Agilent Q-TOF 6510. Single crystal data were collected by Rigaku XtaLAB Synergy. CD spectra were performed on an Applied Photophysics ChirascanV100 model. TEM images were measured on a JEM-1011 electron microscope. SEM pictures were obtained with a G300 FE-SEM scanning electron microscope. The FT-IR spectrum was obtained by an Avatar 370 FT-IR Spectrometer with the KBr pellet method at room temperature. UV-vis curves were obtained at room temperature with a TU-1800pc UV-vis spectrophotometer, a certain concentration of solution was poured into a quartz cuvette to detect the absorption peaks. Fluorescence spectra were measured via a RF-6000 from SHIMADZU. X-ray diffraction (XRD) patterns were collected on a PANalytical (X'Pert3 Powder&XRK-900). Small-angle X-ray Scattering (SAXS) measurement was carried out by an in-house set-up with rotating anode X-ray generator of Rigaku RU 300 with two laterally graded multilayer optics in a side-by-side arrangement, which can give a highly focused parallel beam of mono-chromatic Cu Ka radiation. Density functional theory (DFT) calculation, molecular orbital calculations and electrostatic potential (ESP) surfaces calculations were calculated by B3LYP/6-311G level. Binding

energies of HX derivatives were calculated by B3LYP/def2SVP level. Molecular dynamic (MD) simulation were achieved by the GROMACS 2020 program. The topology files of molecules were parametrized by Amber, ACPYPE, and Guassian tools in GROMACS force field. A box with the volume of 10 × 10 × 10 nm^3 was built firstly. Then 200 HXP (or HXO, HXD) molecules were added into the above box via free dispersing, followed by filling with water (SPC216 model). The MD simulation of HXP self-assembly process was calculated for 20 ns under 298 K. At last, Radical function (RDF) and the number of Hydrogen bonds were calculated through the results based on MD calculation.

4. **Self-assembly process of HX derivatives**

5 mM mother solution of HXO, HXP or HXD were prepared firstly. A certain amount of HXO, HXP or HXD powders were dissolved in THF to get their mother solution (5 mM). Then 200 μL stock solutions (5 mM) of HXO, HXP or HXD in THF were added in a vessel and 1800 μL deionized water was ejected into the above solution.

5. **Solutions of HXO/C_{60}, HXP/C_{60} and HXD/C_{60} in THF/DCB (v/v, 1/1, 0.1 mM) preparation methods**

The above solutions were prepared as below: for example, 1 mM stock solutions of HXO and C_{60} were prepared firstly. A certain amount of HXO powder was dissolved in THF to get HXO stock solution (1 mM), while a certain amount of C_{60} powder was dissolved in DCB to get C_{60} stock solution (1 mM). After that, 100 μL HXO stock solution (1 mM) and 100 μL C_{60} stock solutions (1 mM) were mixed together. Finally, 400 μL THF and 400 μL DCB were added into above solution, and the solution of HXO/C_{60} in THF/DCB (v/v, 1/1, 0.1 mM) was obtained. As for HXP/C_{60} and HXD/C_{60}, the preparation methods were similar with HXO/C_{60}.

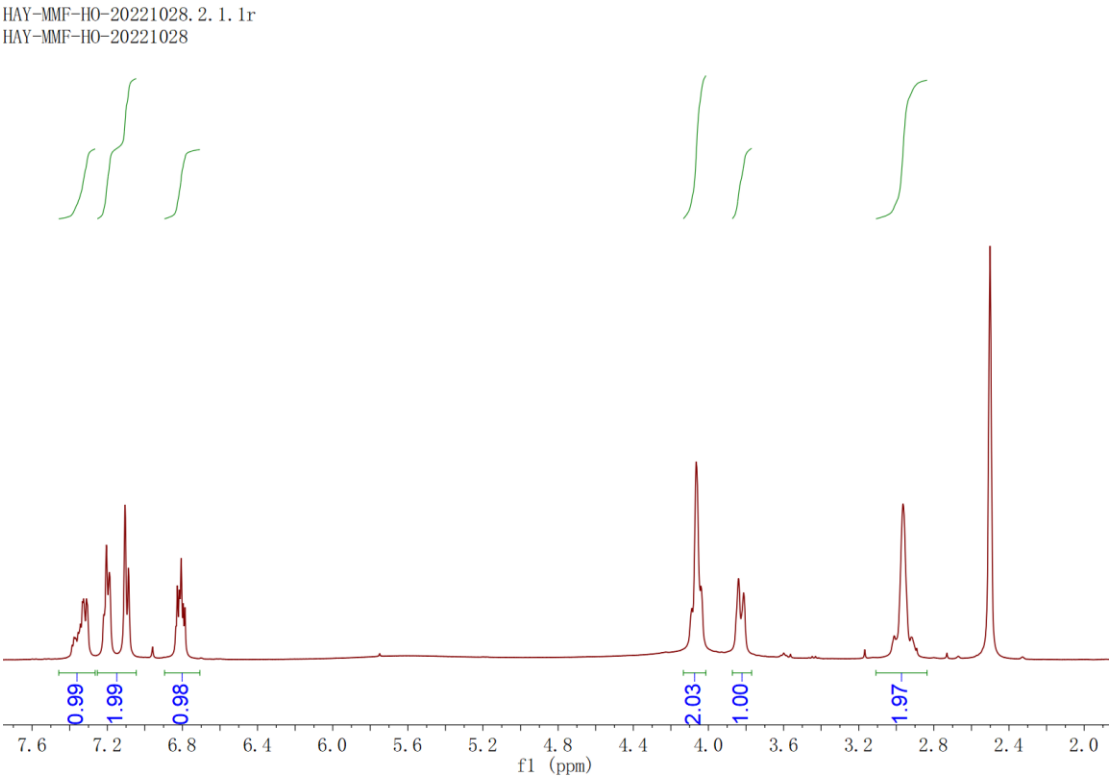


Fig. S2 ^{1}H NMR spectrum (400 MHz) of HXO in Deuterated DMSO.

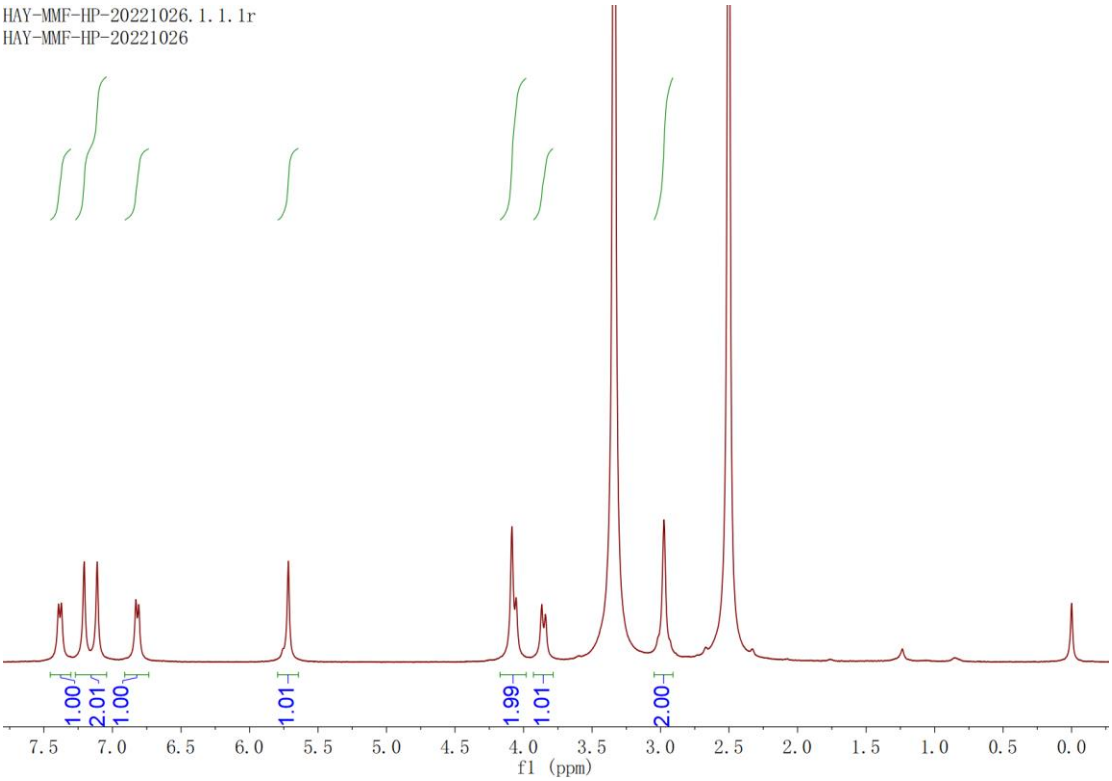


Fig. S3 ^{1}H NMR spectrum (400 MHz) of HXP in Deuterated DMSO.

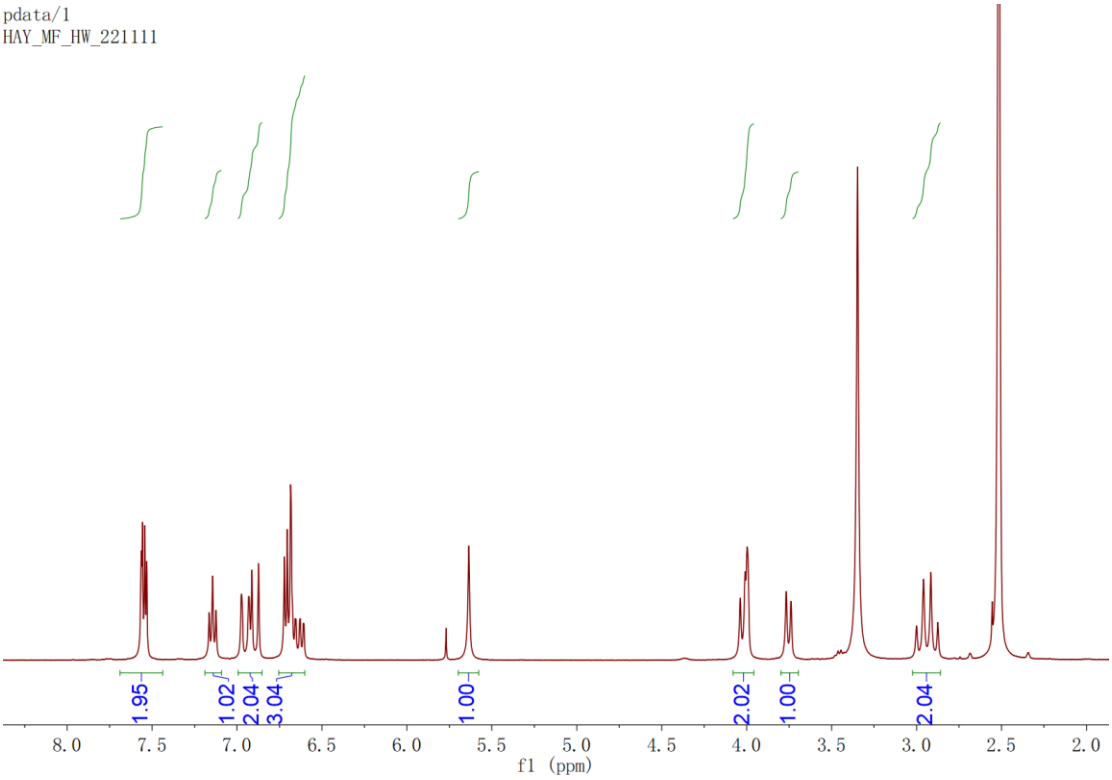


Fig. S4 ^{1}H NMR spectrum (400 MHz) of HXD in Deuterated DMSO.

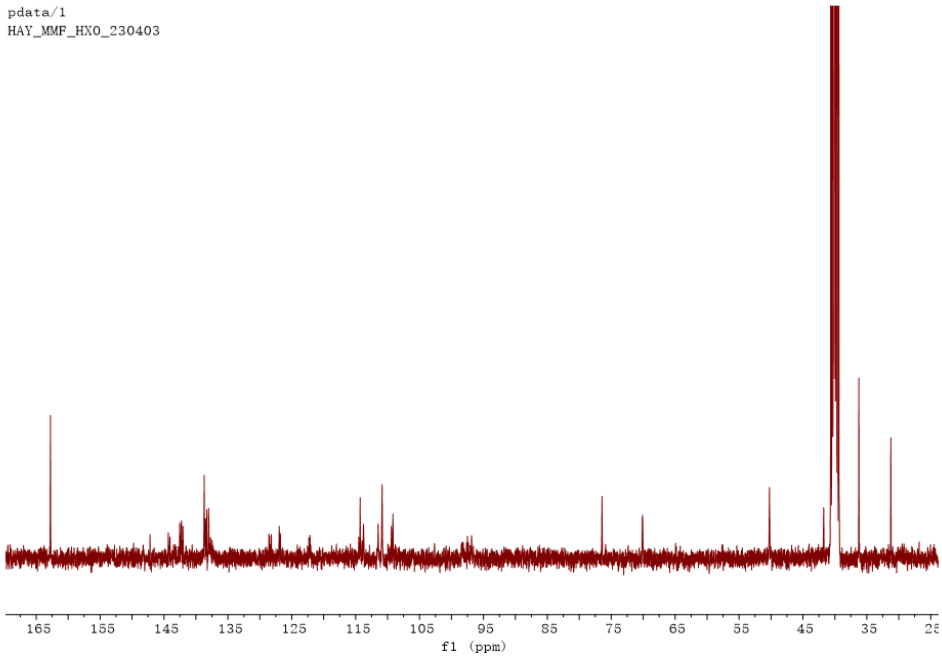


Fig. S5 ^{13}C NMR spectrum (400 MHz) of HXO in Deuterated DMSO.

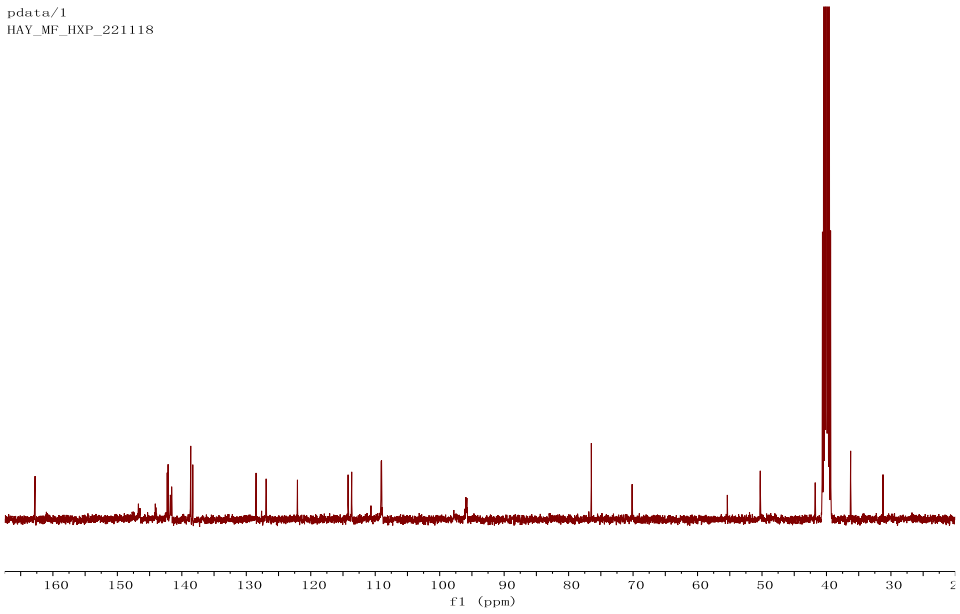


Fig. S6 ^{13}C NMR spectrum (400 MHz) of HXP in Deuterated DMSO.

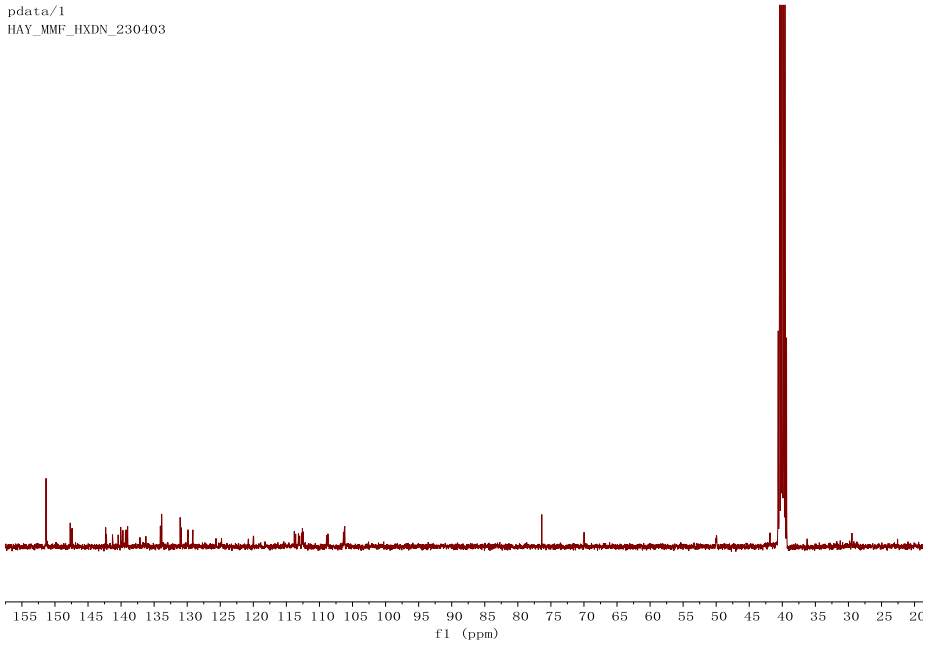


Fig. S7 ^{13}C NMR spectrum (400 MHz) of HXD in Deuterated DMSO.

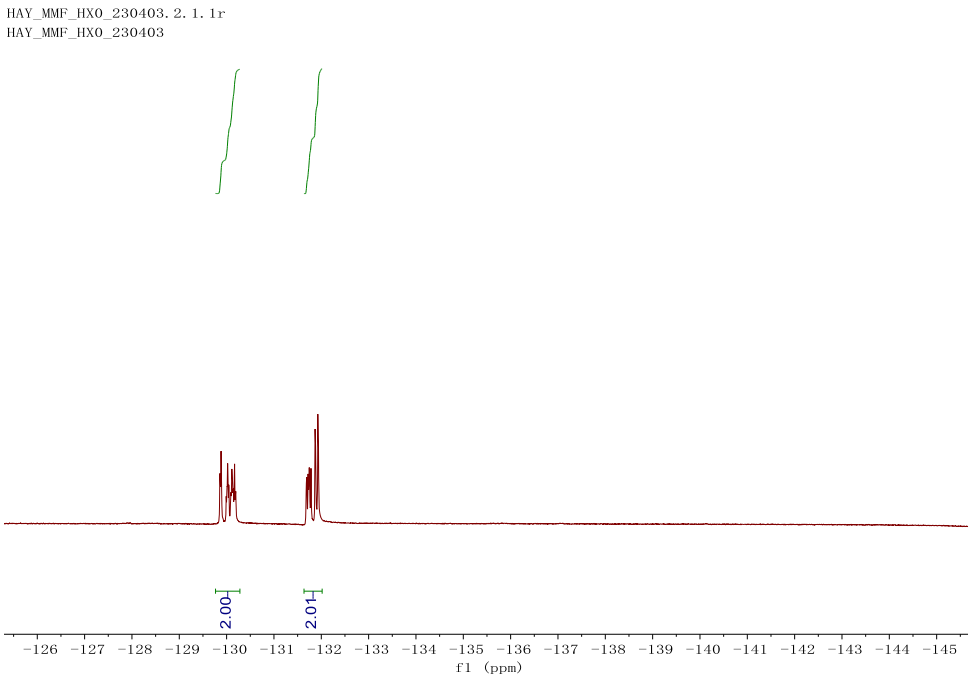


Fig. S8 ^{19}F NMR spectrum (400 MHz) of HXO in Deuterated DMSO.

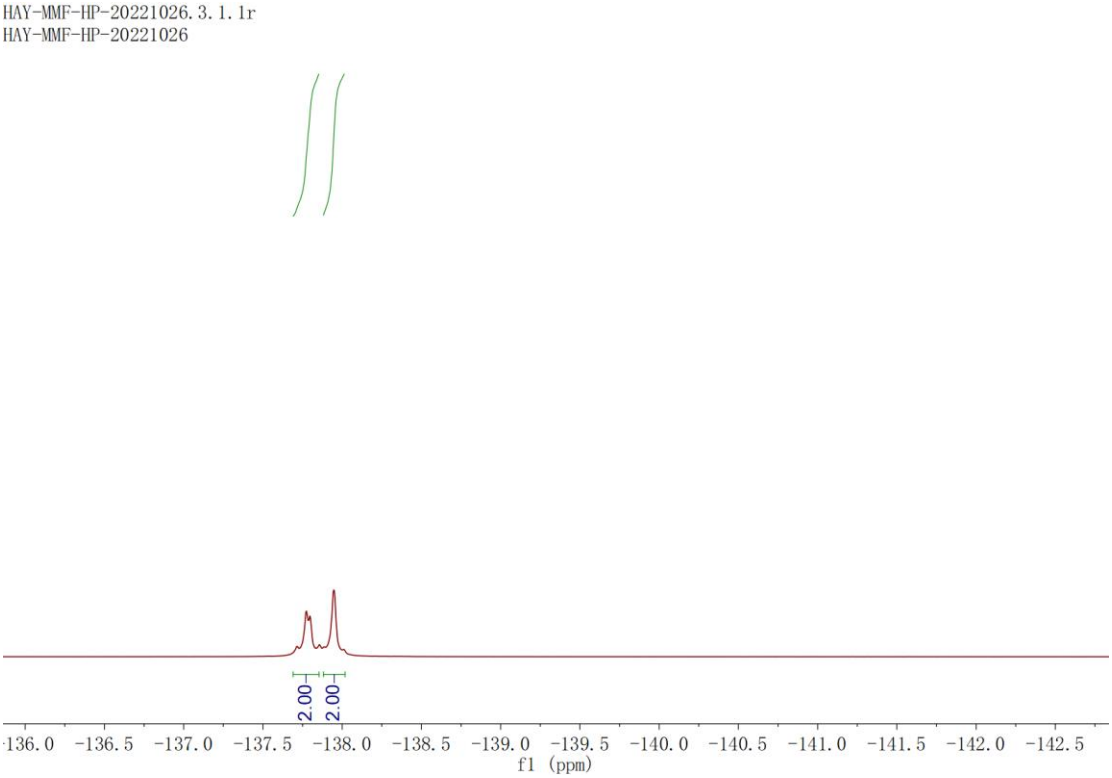


Fig. S9 ^{19}F NMR spectrum (400 MHz) of HXP in Deuterated DMSO.

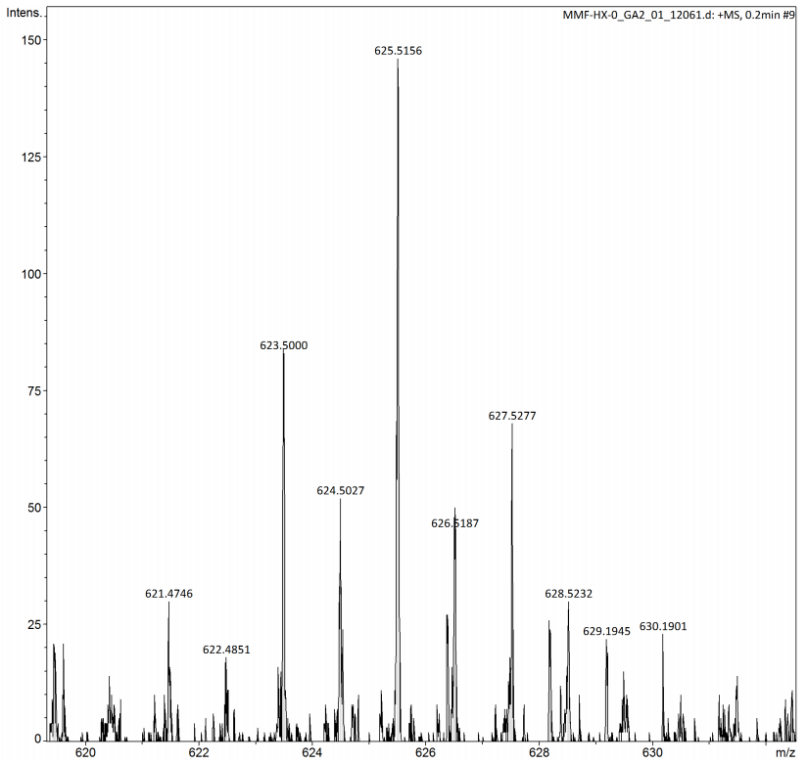


Fig. S10 ESI-MS spectrum of HXO in DMSO.

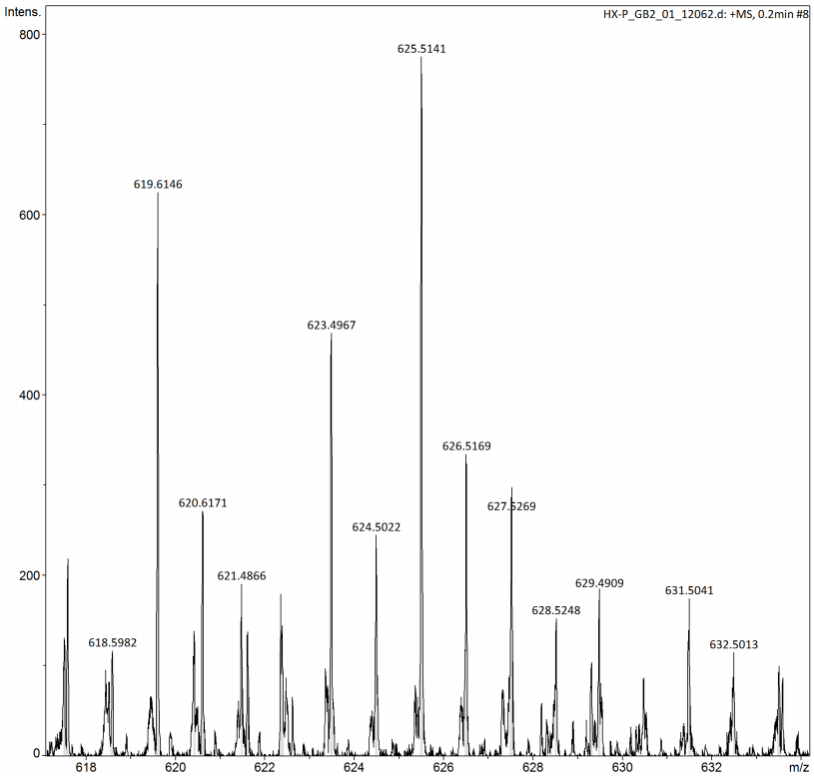


Fig. S11 ESI-MS spectrum of HXP in DMSO.

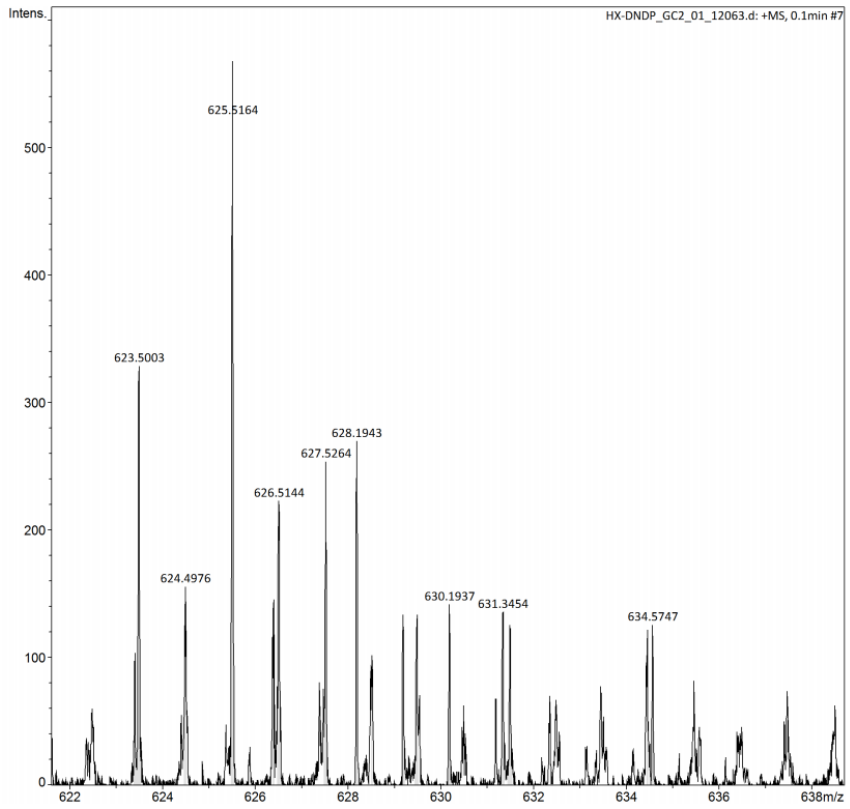


Fig. S12 ESI-MS spectrum of HXD in DMSO.

Deposition Number	2285093
Formula	C_{32} H_9 F_4 N_4 O_6
Space Group	P 2_1 2_1 2_1
Cell lengths	**a** 8.4673(3) **b** 11.7335(6) **c** 28.0005(9)
Cell angles	a 90 b 90 g 90
Cell volume	2781.88
Z, Z’	Z: 4 Z': 0
R-factor(%)	14.1

Table S1: Crystal data of compound HXP.

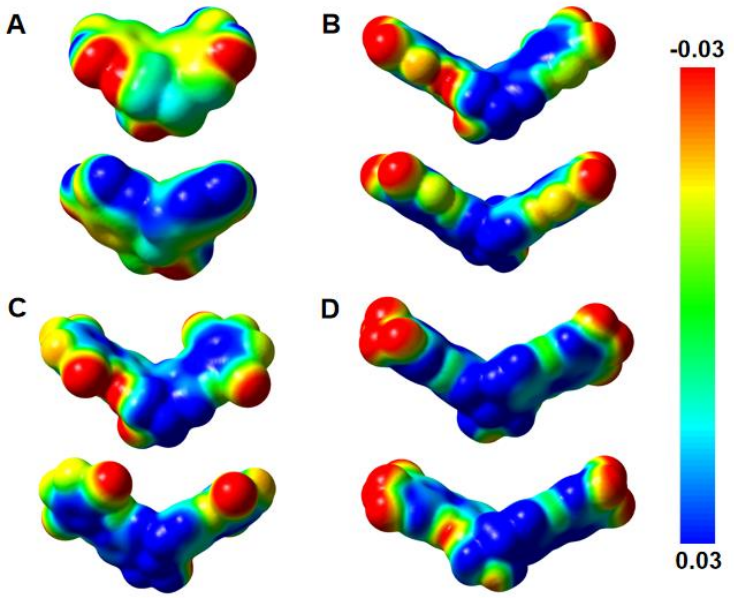


Fig. S13 Electrostatic potential (ESP) surfaces of HX, HXO, HXP and HXD, theory level: B3LYP/6-311G. A: HX; B: HXO; C: HXP; D: HXD.

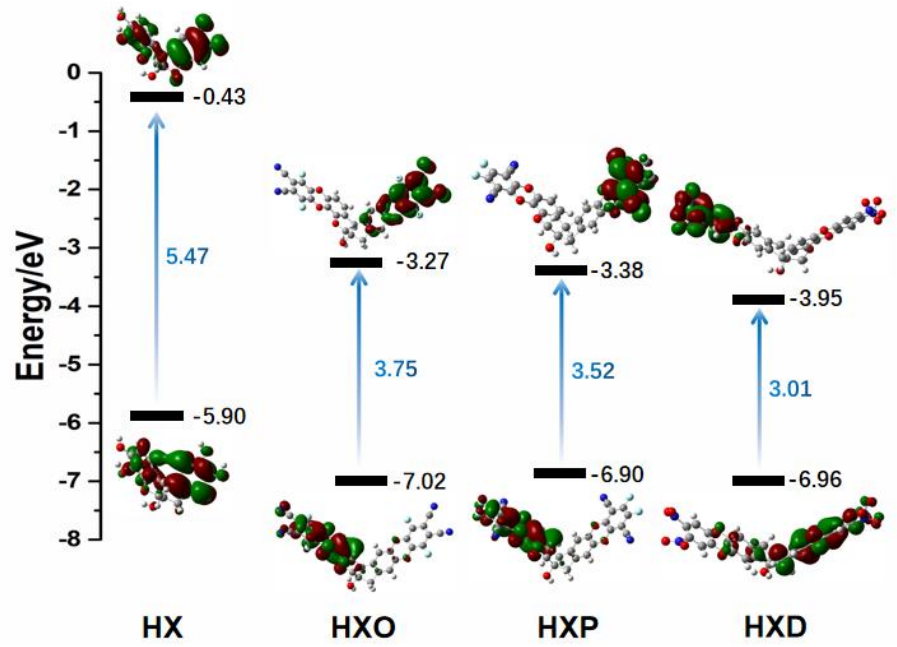
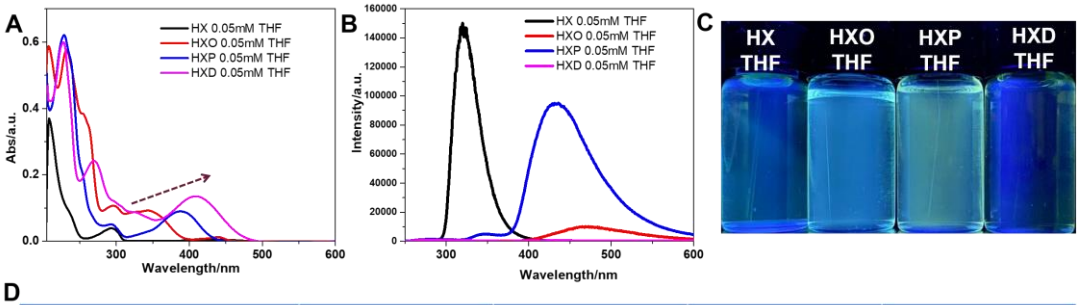


Fig. S14 Calculated HOMO-LUMO energy levels of HX, HXO, HXP and HXD, theory level: B3LYP/6-311G.



D

	HX	HXO	HXP	HXD
Fluorescence quantum yield	22.3%	8.71%	4.28%	0.36%

Fig. S15 A: UV-vis absorption comparison of HX, HXO, HXP and HXD; B: fluorescence emission spectra comparison of HX, HXO, HXP and HXD, excited wavelength of HX and HXO is 207 nm, excited wavelength of HXP and HXD is 228 nm; C: fluorescence emission digital images of HX, HXO, HXP and HXD in THF (the concentrations are all 0.5 mM) under UV light at 365 nm; D: fluorescence quantum yield of HX, HXO, HXP and HXD in THF (the concentrations are all 0.5 mM).

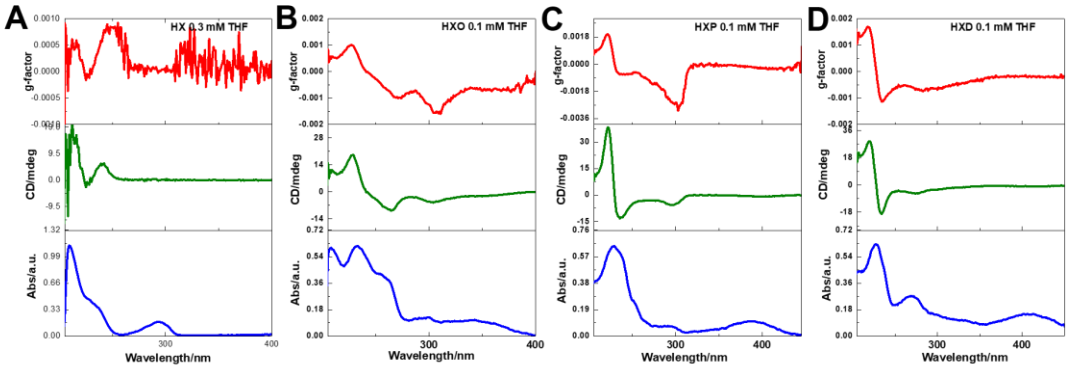


Fig. S16 CD spectra comparison of HX, HXO, HXP and HXD in THF.

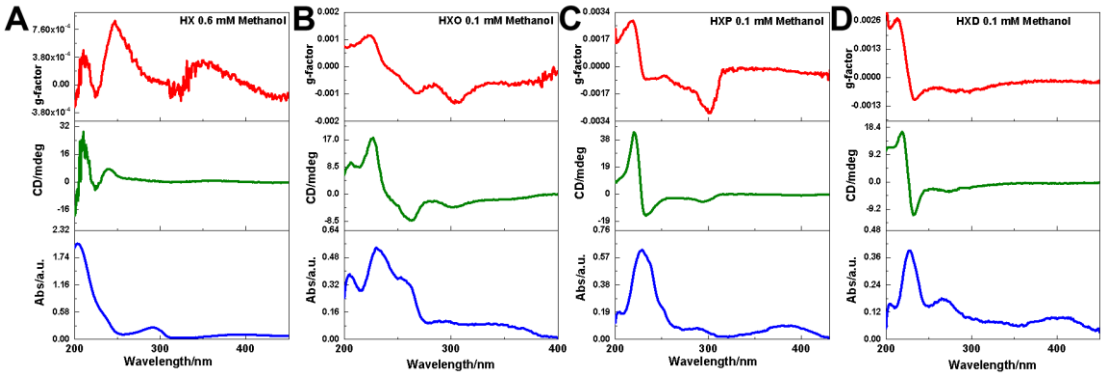


Fig. S17 CD spectra comparison of HX, HXO, HXP and HXD in Methanol.

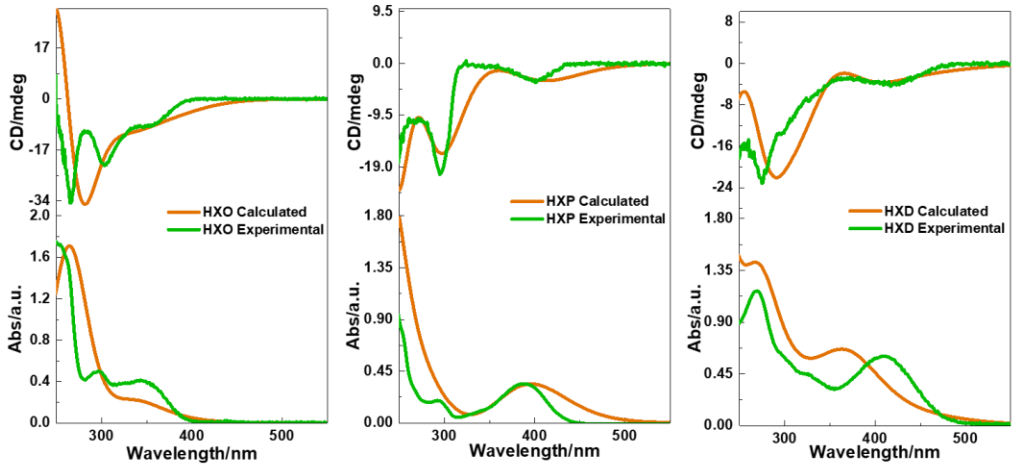


Fig. S18 Electronic circular dichroism (ECD) and experimental CD in THF spectra comparison of HXO, HXP and HXD.

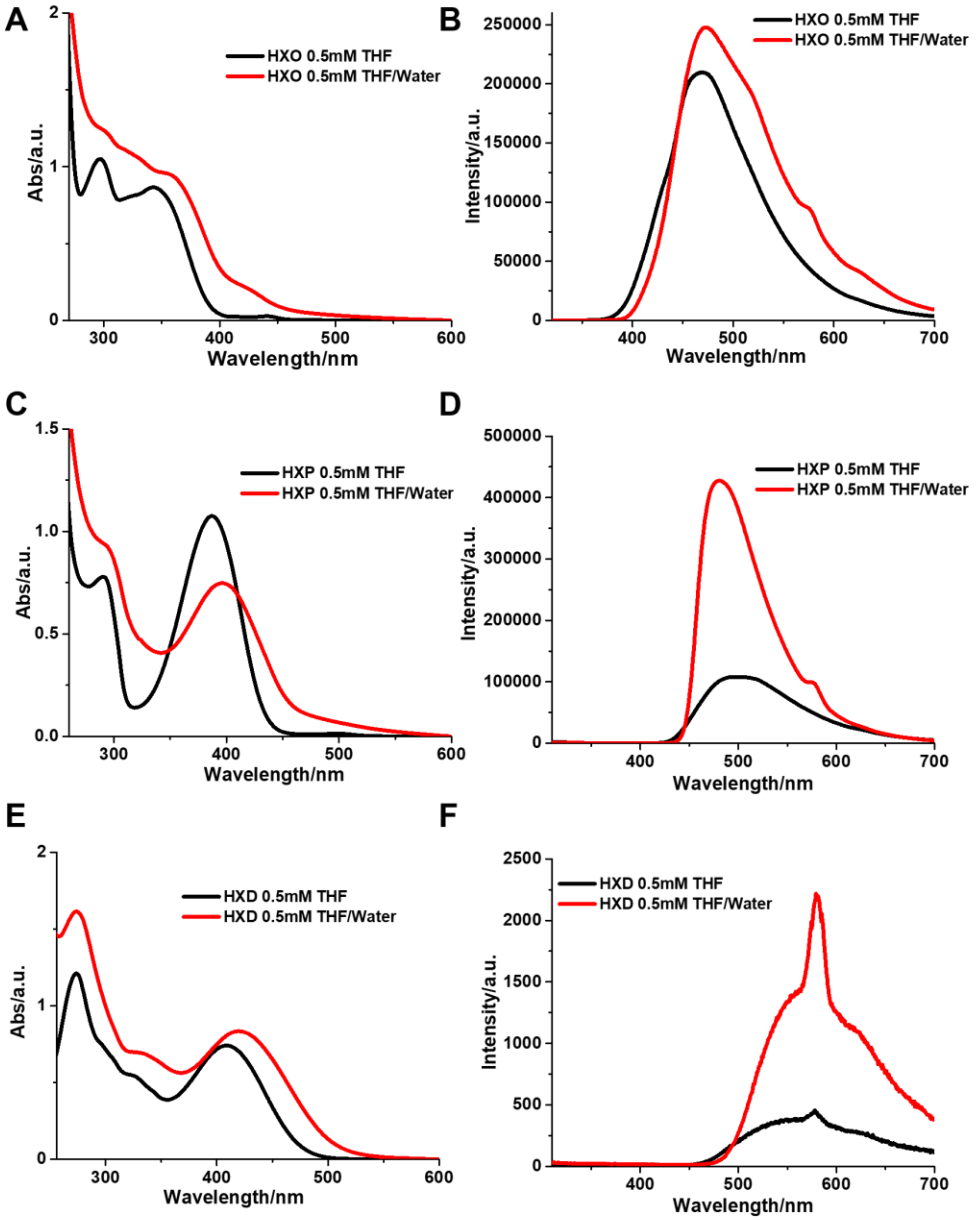


Fig. S19 UV-vis absorption and fluorescence emission spectra comparison of HXO, HXP, HXD in THF and in THF/water (v/v, 1/9), excited wavelength of fluorescence is fixed at 290 nm.

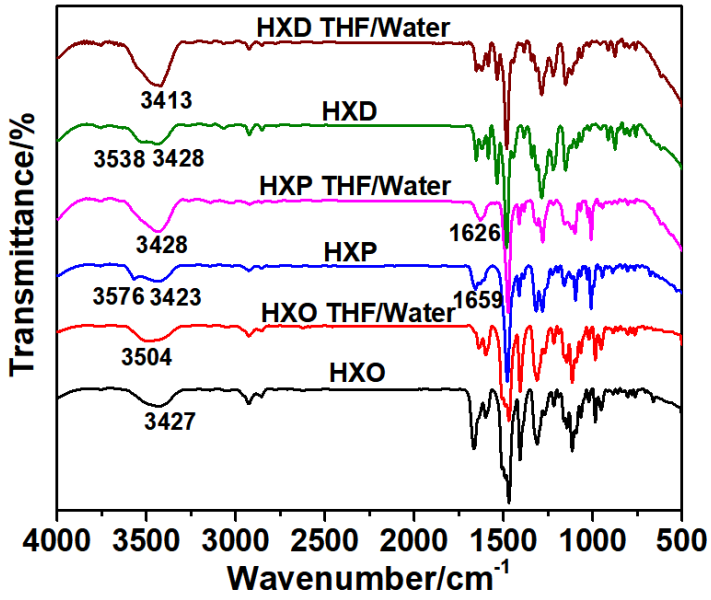


Fig. S20 FT-IR spectra comparison of HXO, HXP, HXD powder and aggregates of HXO, HXP and HXD in THF/water (v/v, 1/9).

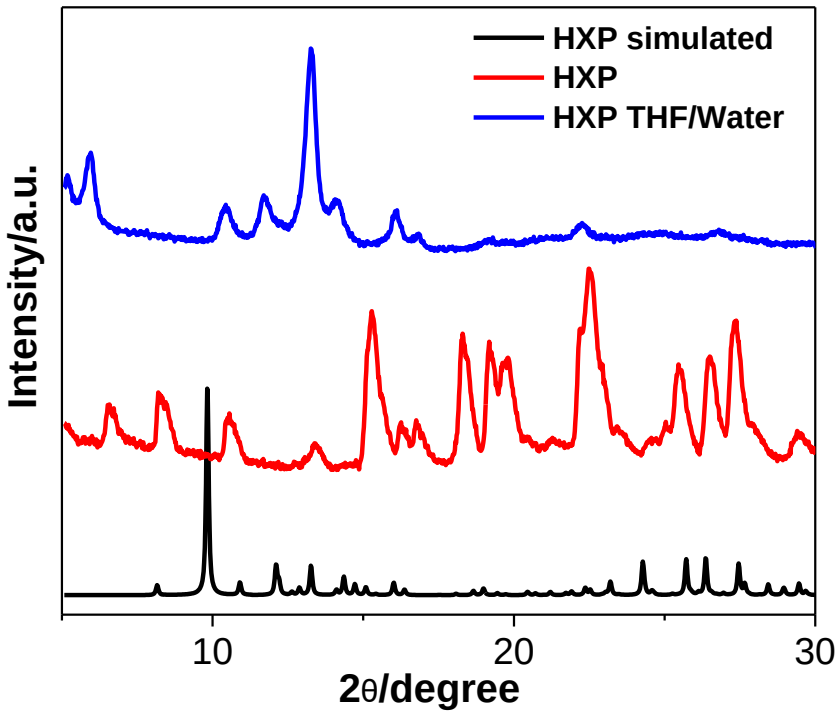


Fig. S21 XRD spectra omparison of HXP simulated, HXP and HXP aggregates in THF/water (v/v, 1/9).

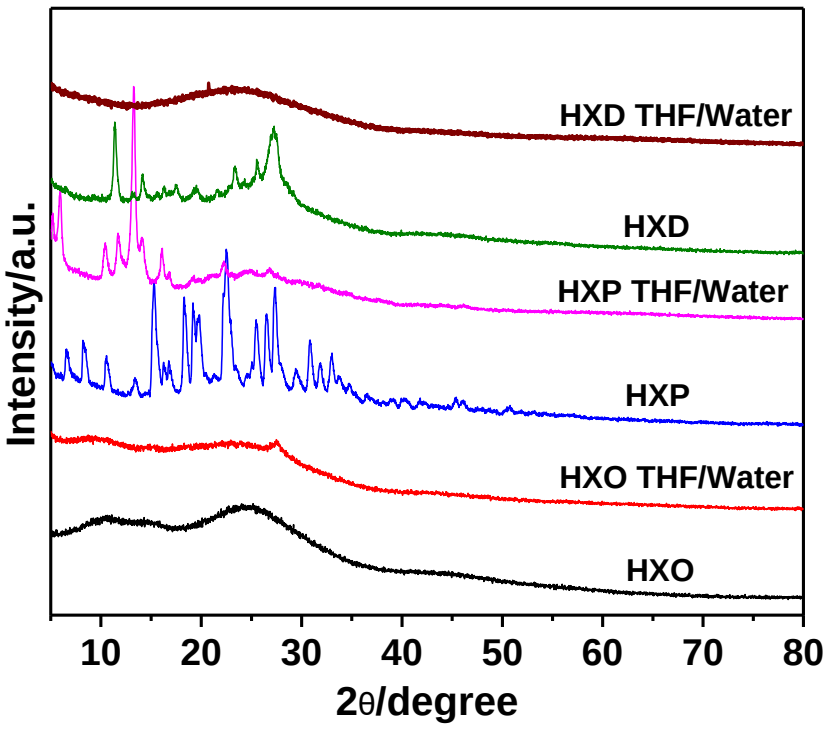


Fig. S22 XRD spectra comparison of HXO, HXP, HXD powder and aggregates of HXO, HXP and HXD in THF/water (v/v, 1/9).

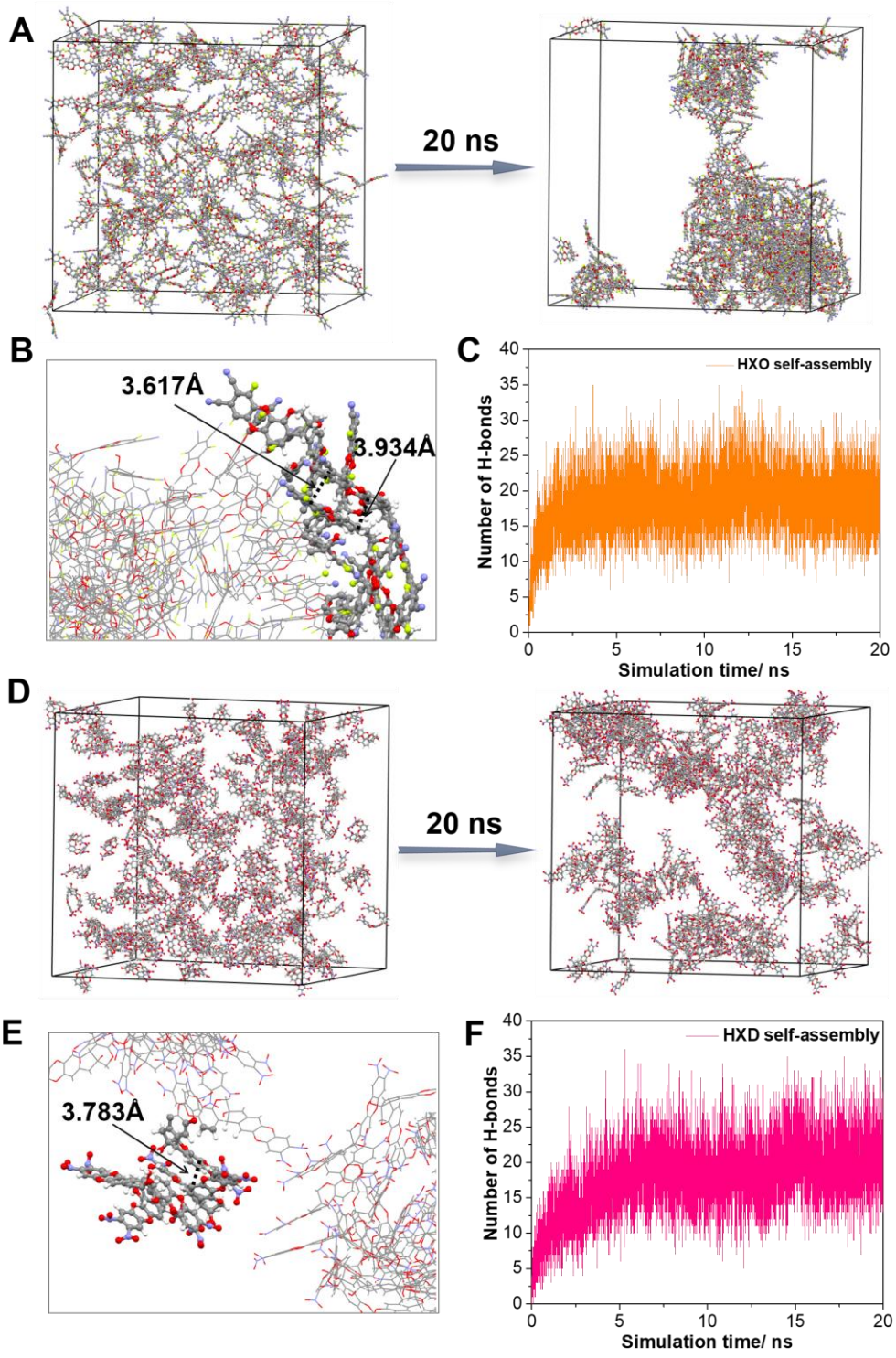


Fig. S23 A: MD simulation result (20 ns) of HXO; B: Partial snapshots of molecular packing mode in MD result of HXO; C: Evolution of the intermolecular hydrogen bonds numbers in HXO self-assembly process along with simulation time; D: MD simulation result (20 ns) of HXD; E: Partial snapshots of molecular packing mode in MD result of HXD; F: Evolution of the intermolecular hydrogen bonds numbers in HXD self-assembly process along with simulation

time.

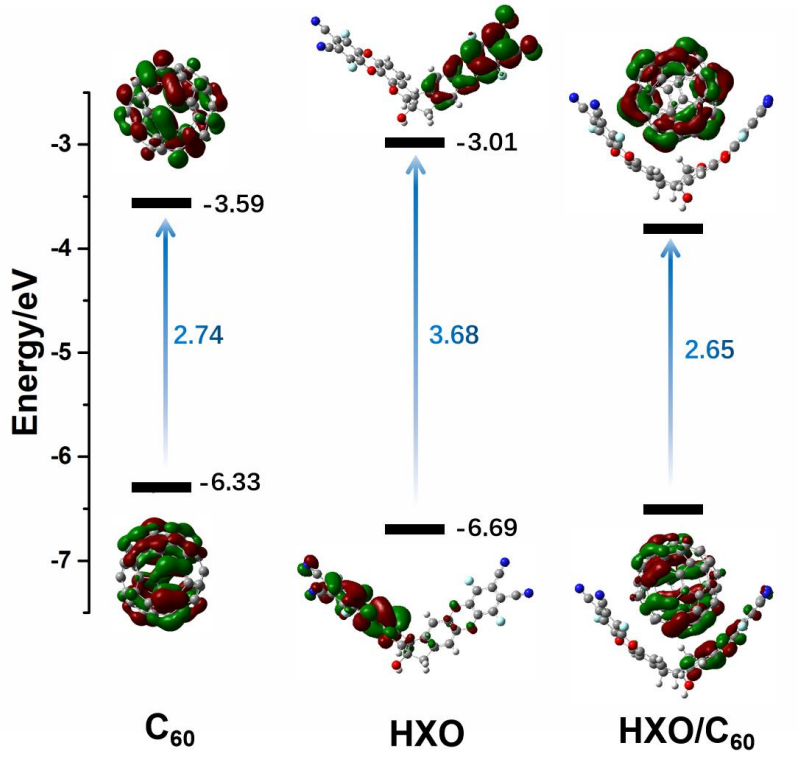


Fig. S24 Calculated HOMO-LUMO energy levels of C_{60}, HXO and HXO/C_{60}, theory level: B3LYP/6-311G.

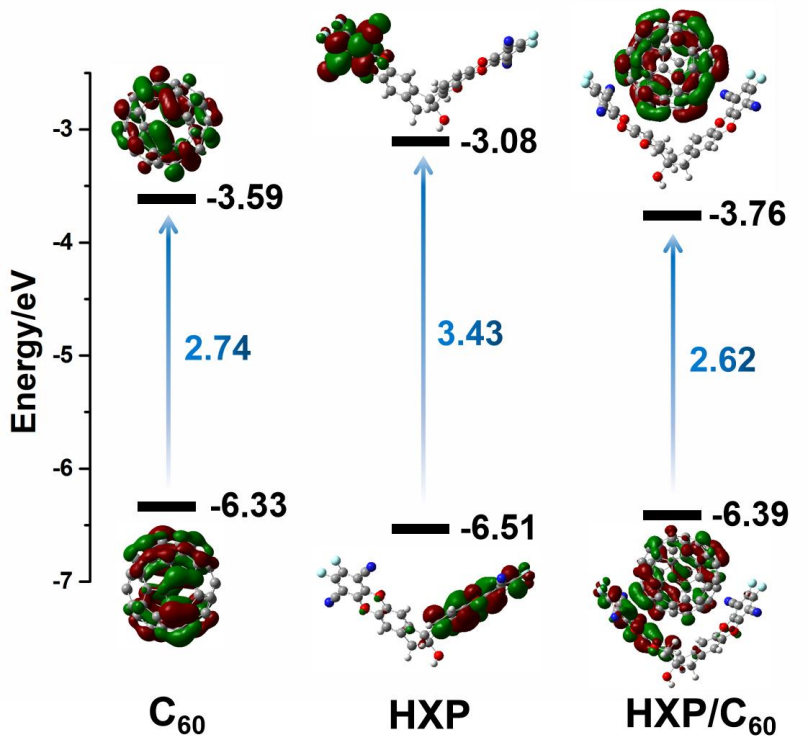


Fig. S25 Calculated HOMO-LUMO energy levels of C_{60}, HXP and HXP/C_{60}, theory level:

B3LYP/6-311G.

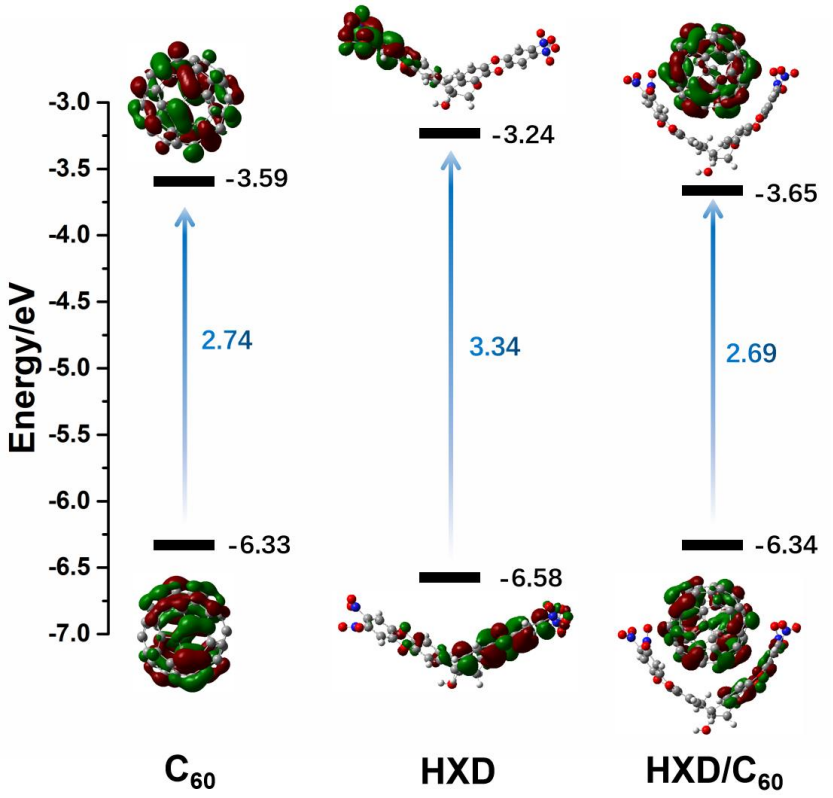


Fig. S26 Calculated HOMO-LUMO energy levels of C_{60}, HXD and HXD/C_{60}, theory level: B3LYP/6-311G.

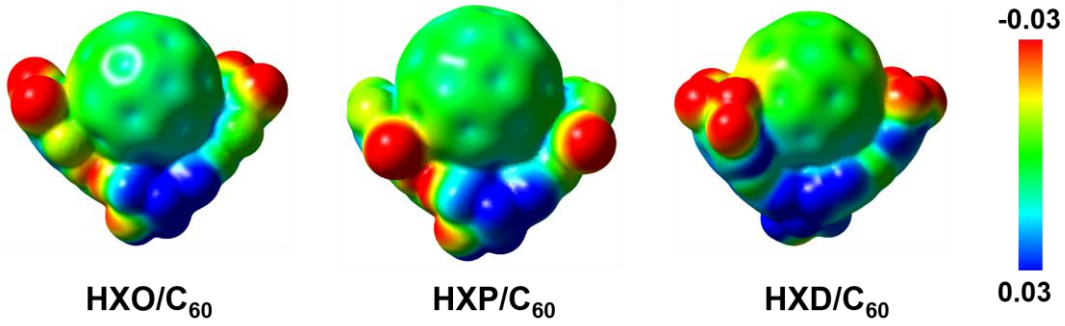


Fig. S27 ESP surfaces of HXO/C_{60}, HXP/C_{60} and HXD/C_{60}, theory level: B3LYP/6-311G.

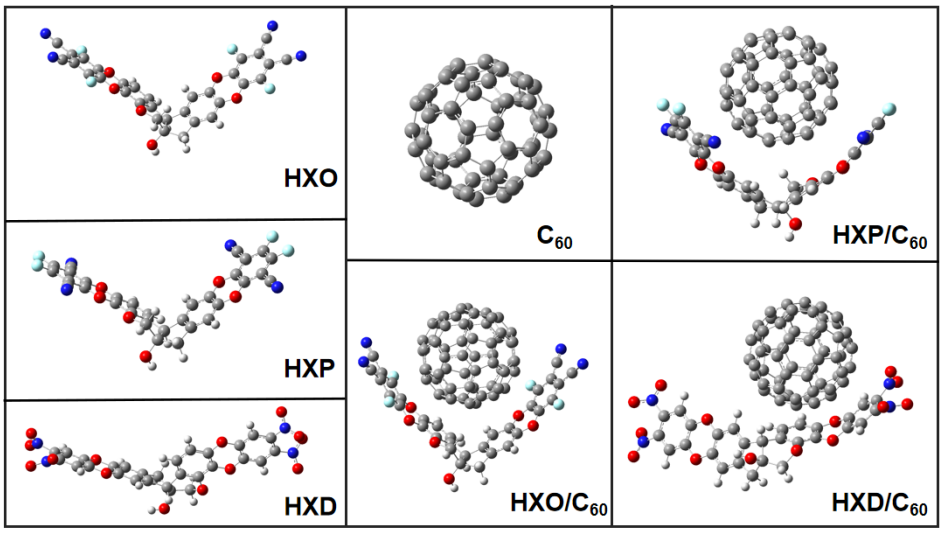


Table S2 Energy optimization results, theory level: b3lyp/def2SVP.

	HXO	HXP	HXD	C_{60}	HXO/C_{60}	HXP/C_{60}	HXD/C_{60}
E (Hartree)	-2293.44	-2293.45	-2345.49	-2284.85	-4578.35	-4578.35	-4630.37

Table S3 Energy values of energy optimization results.

	kcal/mol
$E_{HXO/C60}$	-31.51
$E_{HXP/C60}$	-31.86
$E_{HXD/C60}$	-19.18

Table S4 The binding energies calculated from energy optimization results.

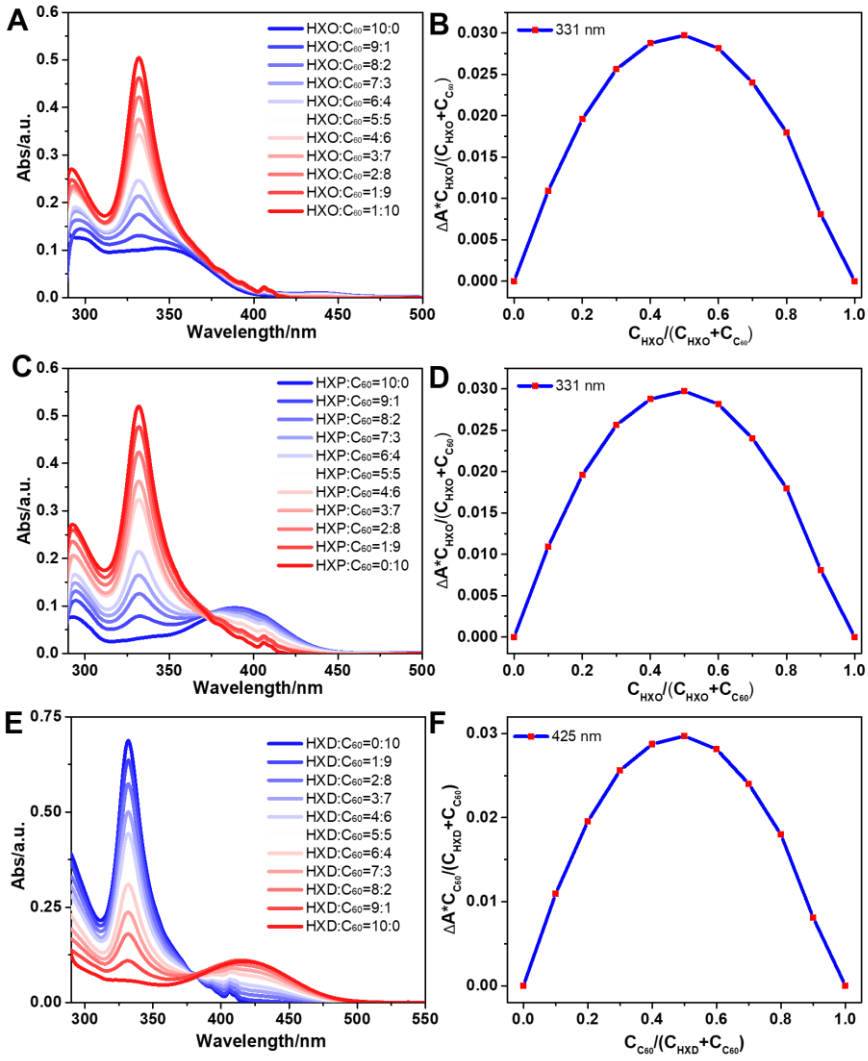


Fig. S28 UV-vis absorption and fluorescence spectra in THF/DCB (v/v, 1/1) comparison with the ratio from 0: 10 to 10:0 between host and guest molecules, A) HXO/C_{60}; C) HXP/C_{60}; E) HXD/C_{60}. Job's plots, B) HXO/C_{60}; D) HXP/C_{60}; F) HXD/C_{60}.

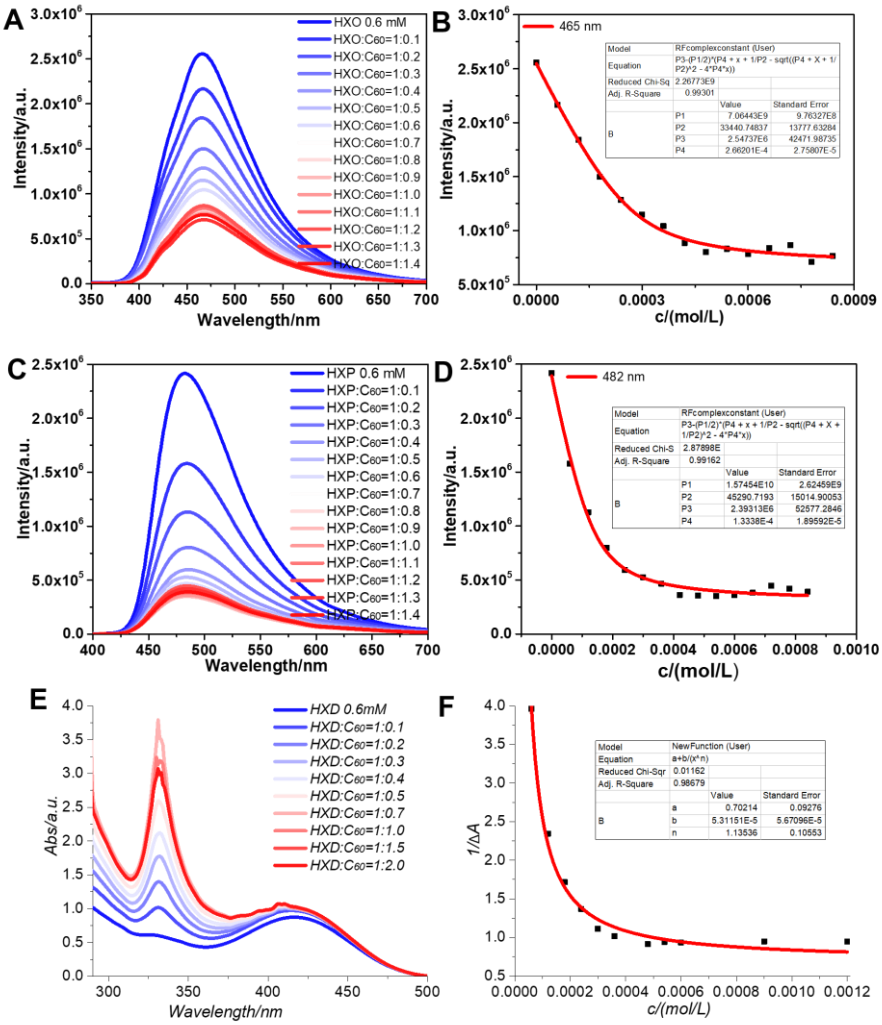


Fig. S29 UV-vis absorption and fluorescence spectra in THF/DCB (v/v, 1/1) comparison upon increasing the ratio of C_{60}, A) HXO/C_{60}; C) HXP/C_{60}; E) HXD/C_{60}. Simulation curves, B) HXO/C_{60}; D) HXP/C_{60}; F) HXD/C_{60}.

Method	K	n	R^2
UV	$K_{HXD/C60}$= ***13219.38 M^{-1}***	1.135	0.98679
RF	$K_{HXO/C60}$= ***33440.75 M^{-1}***	1:1	0.99301
	$K_{HXP/C60}$= ***45290.72 M^{-1}***	1:1	0.99162

Table S5 The binding constants of HXO/C_{60}, HXP/C_{60} and HXD/C_{60}.

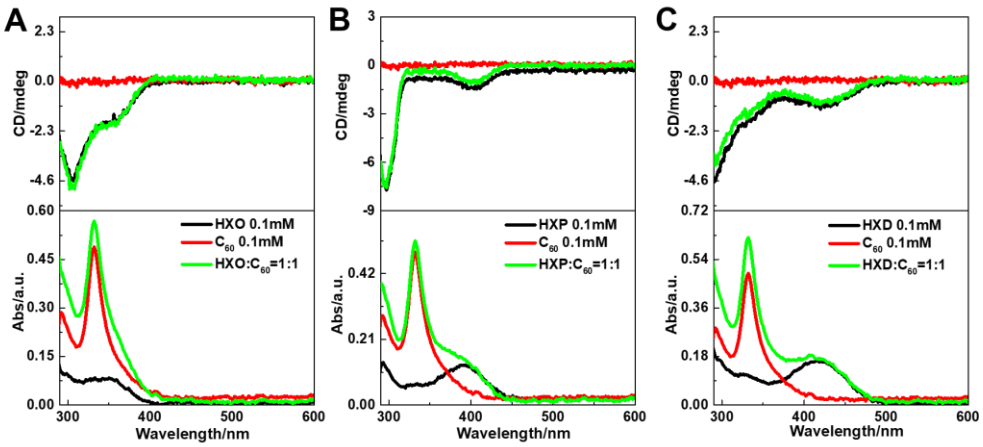


Fig. S30 CD spectra comparison of HXO/C_{60}, HXP/C_{60} and HXD/C_{60} in THF/DCB (v/v, 1/1).

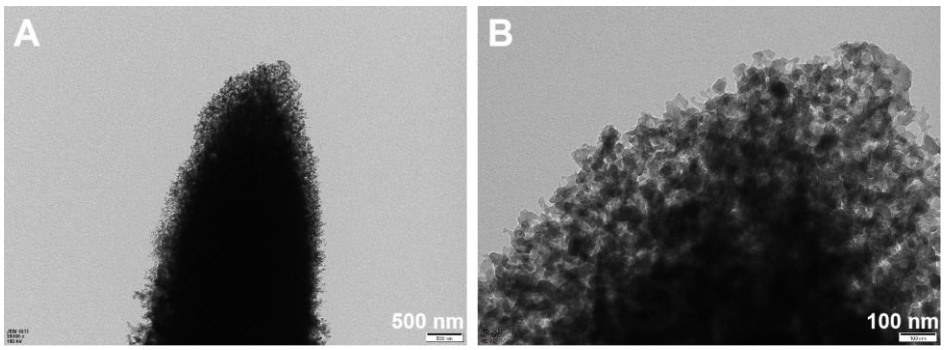


Fig. S31 TEM images of C_{60} (0.1 mM) in THF/DCB (v/v, 1/1), A) scale bar = 500 nm; B) scale bar = 100 nm.

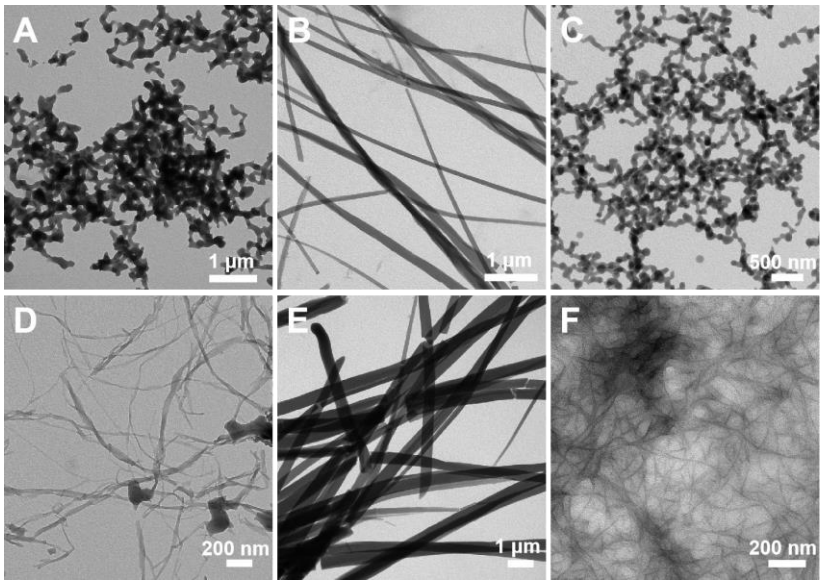


Fig. S32 TEM images of self-assemblies in THF/DCB (v/v, 1/1). A) HXO (0.1 mM), scale bar = 1 μm;

B) HXP (0.1 mM), scale bar = 1 µm; C) HXD (0.1 mM), scale bar = 500 nm; D) HXO/C_{60} (0.1 mM), scale bar = 200 nm; E) HXP/C_{60} (0.1 mM), scale bar = 1 µm; F) HXD/C_{60} (0.1 mM), scale bar = 200 nm.

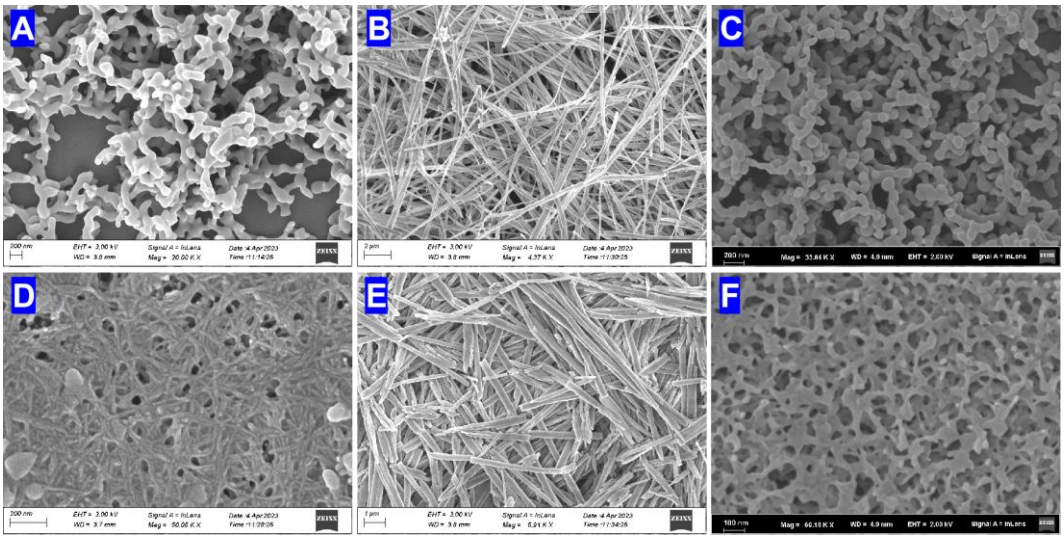


Fig. S33 SEM images of self-assemblies in THF/DCB (v/v, 1/1). A) HXO (0.1 mM), scale bar = 200 nm; B) HXP (0.1 mM), scale bar = 2 µm; C) HXD (0.1 mM), scale bar = 200 nm; D) HXO/C_{60} (0.1 mM), scale bar = 200 nm; E) HXP/C_{60} (0.1 mM), scale bar = 1 µm; F) HXD/C_{60} (0.1 mM), scale bar = 100 nm.