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Bis-Pyrene-Based Supramolecular Aggregates with Reversibly Mechanochromic and Vapochromic Responsiveness

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Materials. All reagents and solvents were purchased from commercially available sources and used without further purification.

Instrument and measurements. ^{1}H NMR spectra were recorded on an Advance Bruker 400M spectrometer in deuterated chloroform. Chemical shifts are quoted in parts per million (ppm) and referenced to tetramethylsilane. The ^{13}C NMR spectra were recorded at 100 MHz on the same spectrometer in deuterated chloroform. Chemical shifts were defined relative to the ^{13}C resonance shift of chloroform (77.0 ppm). The UV absorption was determined with a Shimadzu 2600 UV/vis spectrometer. Fluorescence spectrum was recorded on F-280 spectrometer from Tianjin Gangdong Sci&Tech. Development. Co., Ltd. Microflex LRF MALDI-TOF was used to determine the molecular mass. High-resolution mass spectrometry was taken on a GCT Premier from Waters Co. Time-resolved fluorescence spectra were measured with Edinburgh Analytical Instruments F900 (Edinburgh Instruments). The powder X-ray diffraction (XRD) was measured on D/MAX-TTRIII (CBO). SEM was measured on High Resolution Field Emission Scanning Electron Microscopy of NOVA NanoSEM 430. The absolute fluorescence quantum yields were determined by Nanolog (HORIBA).

Synthesis: General Friedel-Crafts acylation procedure: Pyrene (2.02 g, 10.00 mmol) and alkyl dichloride or aryl chloride (5.00 mmol) were dissolved in dichloromethane (50 mL), and the mixture was cooled to 0 °C. After the portion-wise addition of $AlCl_3$ (2.00 g, 15.00 mmol), the mixture was allowed to react overnight at room temperature, and then the mixture was poured into ice-water and stirred until the color of the organic phase turned from black to yellow. The aqueous phase was extracted with dichloromethane. The combined organic phases were dried with $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography.

Compound *m*-BP: This compound was prepared according to the general procedure and obtained as yellow solid (silica gel, CH_2Cl_2:hexane 3/1 as eluent, 1.62 g, 60.7%). ^{1}H NMR: 8.40 (d, J = 9.2 Hz, 2H), 8.32 (s, 1H), 8.24 (t, J = 7.5 Hz, 4H), 8.18 (dd, J = 7.8, 1.7 Hz, 2H), 8.13 (dd, J = 9.1, 5.8 Hz, 4H), 8.09-7.97 (m, 8H), 7.64 (t, J =

7.7 Hz, 1H). ^{13}C-NMR: 198.28, 140.15, 135.46, 134.28, 133.52, 132.90, 132.04, 131.52, 130.84, 130.28, 130.06, 139.81, 128.03, 127.39, 127.17, 127.00, 125.72, 125.49, 125.24, 124.67. MALDI-TOF: calcd. for $C_{40}H_{22}O_2$ 534. 16, found $M+H^+$ 535.05. HRMS: calcd. for $C_{40}H_{22}O_2$ 534.1620, found M^+ 534.1620.

Compound *p*-BP: This compound was prepared according to the general procedure and obtained as yellow solid (CH_2Cl_2:hexane 2/1 as eluent,1.21 g, 44.81%). ^{1}H NMR: 8.47 (d, J = 9.2 Hz, 2H), 8.28 (dd, J = 7.4, 5.5 Hz, 4H), 8.24-8.08 (m, 12H), 8.00 (s, 4H). ^{13}C NMR spectrum was not available due to the low solubililty of compound. MALDI-TOF: calcd. for $C_{40}H_{22}O_2$ 534.16, found M^+ 534.88. HRMS: calcd. for $C_{40}H_{22}O_2$ 534.1620, found M^+ 534.1620.

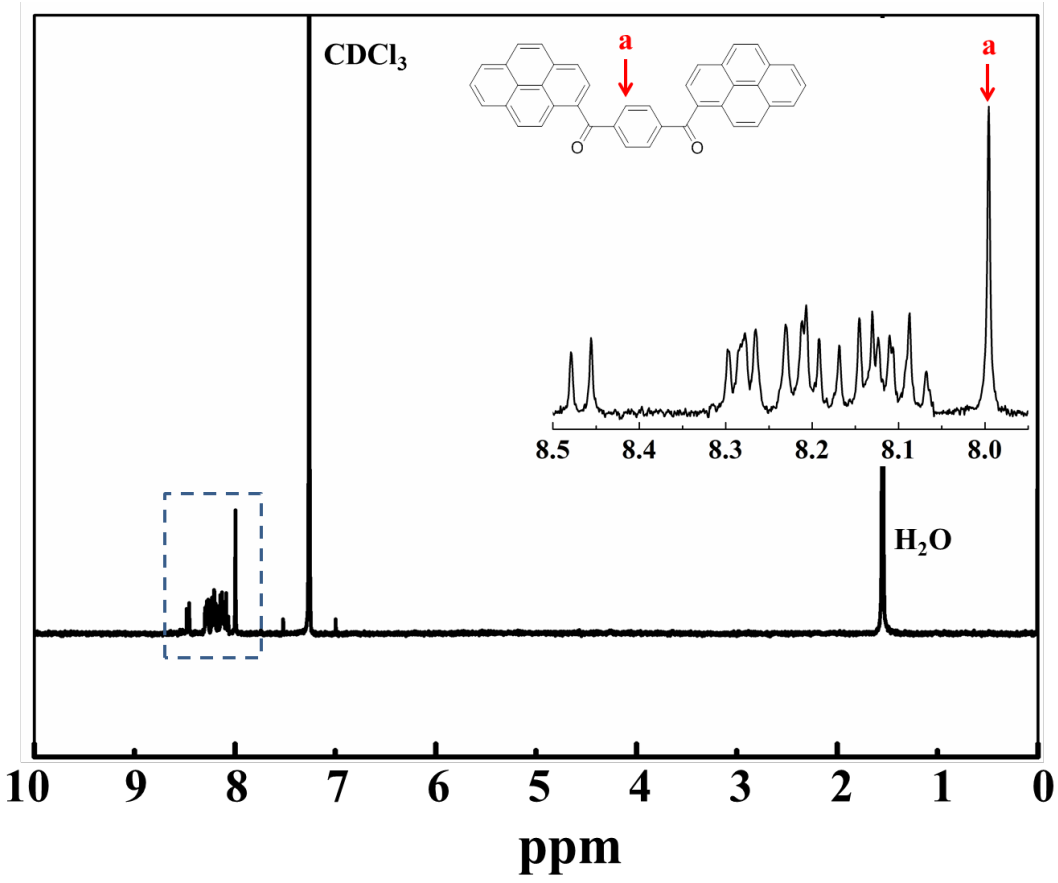


Figure S1 ^{1}H NMR spectrum of compound ***p*-BP** in $CDCl_3$. The inset represents a zoom of the NMR region 7.95–8.5 ppm and shows the characteristic NMR signals of ***p*-BP**.

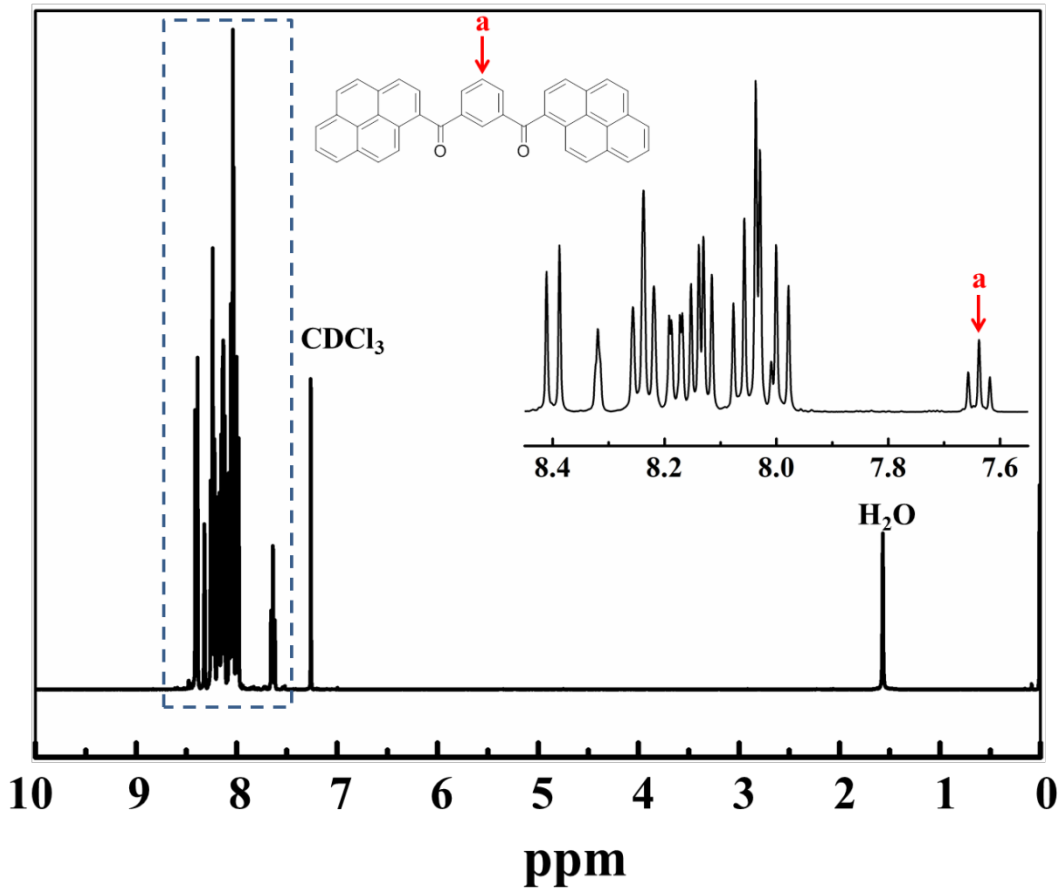


Figure S2.^{1}H NMR spectrum of compound ***m*-BP** in $CDCl_3$. The inset represents a zoom of the NMR region 7.55–8.45 ppm and shows the characteristic NMR signals of ***m*-BP.**

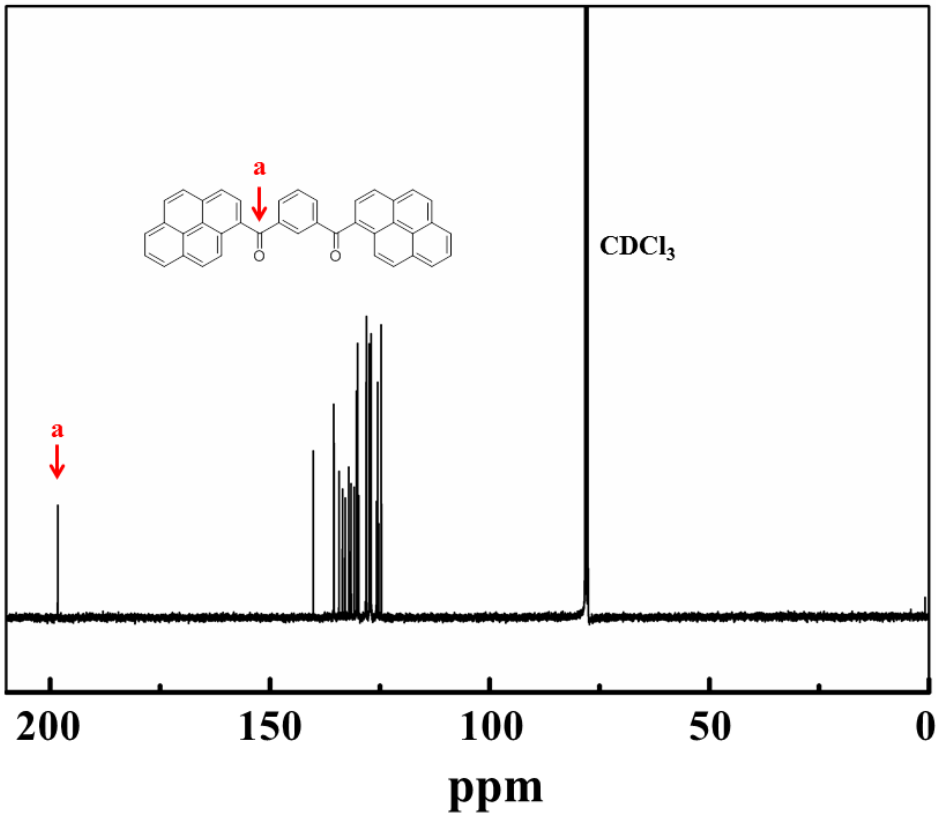


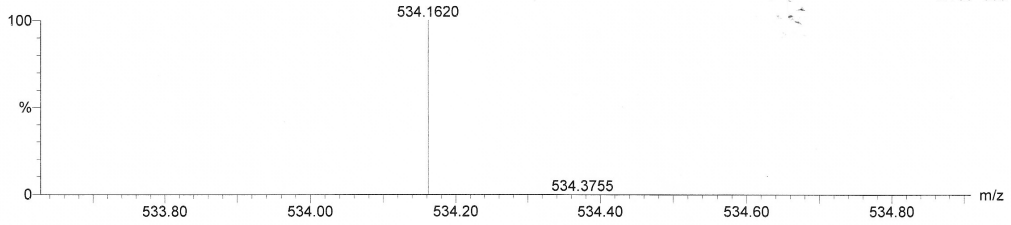
Figure S3. ^{13}C NMR spectrum of compound ***m*-BP** in $CDCl_3$.

Elemental Composition Report Page 1

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
120 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-45 H: 0-23 N: 0-3 O: 0-4 Si: 0-2
4
LV4 270 (4.501) Cm (259:270-(248:253+288:289))

TOF MS EI+
2.76e+005



Minimum:	80.00				-1.5					
Maximum:	100.00		2.0	10.0	50.0					
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula			
534.1620	100.00	534.1620	0.0	0.0	30.0	5684220.5	C40	H22	O2	
		534.1606	1.4	2.6	30.5	5684225.5	C38	H20	N3	O

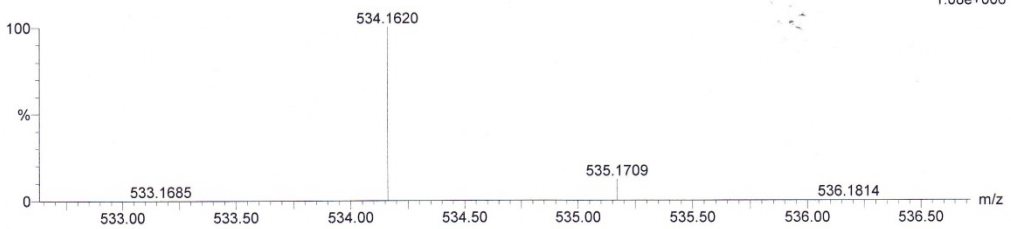
Figure S4. The EI-MS spectrum of compound ***p*-BP**.

Elemental Composition Report Page 1

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
30 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-45 H: 0-23 O: 0-4 Si: 0-2
1
LV1 447 (7.451) Cm (447:470-(407:409+471))

TOF MS EI+
1.08e+006



Minimum:	80.00				-1.5				
Maximum:	100.00		2.0	10.0	50.0				
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula		
534.1620	100.00	534.1620	0.0	0.0	30.0	472403.6	C40	H22	O2

Figure S5.The EI-MS spectrum of compound ***m*-BP**.