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Supporting Information

Self-reversible mechanofluorochromism of AIE-active C6-unsubstituted tetrahydropyrimidine derivatives

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CONTENTS

1. Characterization data for THP 2

The crystals of **2** were prepared by recrystallization from dichloromethane/n-hexane solution. The characterization data for **2** is shown as below.

THP **2** (Dimethyl 1,2,3-tris(4-(trifluoromethyl)phenyl)-1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylate): 35% yield, white solid, m.p. 189-190 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.74 (s, 4H), 7.51 (m, 4H), 7.02 (m, 4H), 6.29 (s, 1H), 4.39 (d, J = 18.2 Hz, 1H), 3.66 (m, 7H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.9, 164.2, 151.1, 146.9, 142.5, 140.8, 127.1, 126.8, 126.5, 122.3, 117.2, 105.9, 77.5, 53.0, 51.8, 43.0 ppm; IR (KBr) ν (cm^{-1}): 2921, 2851, 1703, 1627, 1517, 1425, 1322, 1239, 1167, 1069, 918, 837, 753, 698; HRMS-ESI (m/z): calcd for $C_{29}H_{21}O_4N_2F_9Na$, $[M+Na]^+$: 655.1250; found, 655.1248.

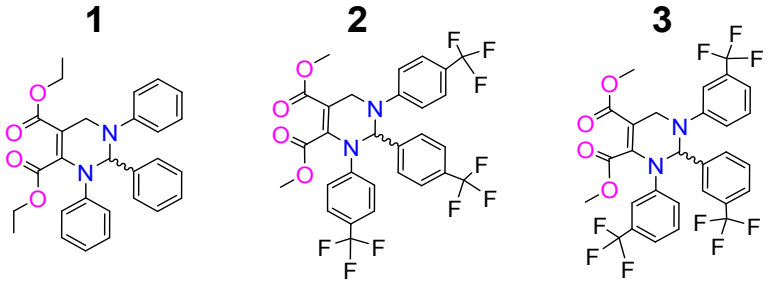
2. Crystallographic data for THPs 2 and 3

Table S1 Crystallographic data for THPs **2** and **3**

THP	**2**	**3**
T [K]	149.99	187.49
crystal system	Orthorhombic	Monoclinic
space group	*P*bca	*P*121/n1
a[Å]	11.6160(4)	14.2291(17)
b[Å]	20.6335(7)	11.4539(14)
c[Å]	23.3007(7)	17.931(2)
α[Å]	90	90
β[deg]	90	105.852(2)
γ[deg]	90	90
V [Å^3]	5584.7(3)	2811.2(6)
Z	8	4
D_{calcu} [mg/m^3]	1.504	1.494
R	0.0842	0.0731
wR_2	0.2085	0.1120

3. Intra- and intermolecular interactions in THPs 1-3

Table S2 Intra- and Intermolecular short-ring interactions and hydrogen bonds in THPs **1-3**

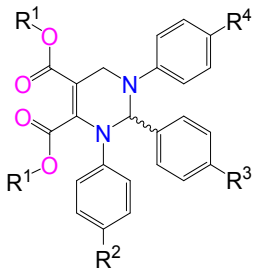


THP	polymorph	Intermolecular short ring-interactions[a]	Intramolecular short ring-interactions[a]	Intermolecular hydrogen bonds	Intramolecular hydrogen bonds
1	**1b**	A-B', 5.035 Å A-C', 5.122 Å B-C', 4.938 Å	A-C, 5.805 Å	2 × C-H...O, 2.487 Å 6 × C-H...π, 2.930 Å; 2.837 Å; 2.971 Å	C-H...N, 2.505 Å C-H...O, 2.578 Å
	1c	A-B" and A'-B, 5.293 Å B-C' and B"-C, 4.257 Å	A-C, 5.039 Å	4 × C-H...O, 2.434 Å; 2.579 Å 2 × C-H...π, 2.634 Å	C-H...N, 2.511 Å
2		A'-B, 5.476 Å B-C', 4.754 Å	A-C, 5.098 Å	2 × C-H...O, 2.453 Å; 2.321 Å C-H...F, 2.550 Å 3 × C-F...π, 3.236 Å; 3.517 Å; 3.477 Å	C-H...N, 2.501 Å
3		C-B', 4.103 Å, C-A", 5.408 Å A-B', 4.800 Å B'-A", 5.928 Å C"-A"', 5.874 Å	A-C, 5.199 Å	C-H...π, 2.847 Å C-H...O, 2.432 Å C-H...F, 2.459 Å	C-H...N, 2.469 Å C-H...O, 2.583 Å C-H...F, 2.411 Å

[a] The lengths are the distances (d_{ring}) between ring centroids.

4. Molecular packing modes of the polymorphs of THPs with different R^1–R^4 in single crystals and their emissions

Table S3 MPMs of the polymorphs of THPs with different R^1–R^4 in single crystals and their emissions



entry	THP	R^1	R^2	R^4	R^3	MPM[a]	λ_{em}[b]/nm
1	**1b**	Et	Ph	Ph	Ph	*RS*-paired	434
2	**1c**	Et	Ph	Ph	Ph	*RR*/*SS*-overlapped	484
3	**4c**	Me	Ph	Ph	Ph	*RS*-paired	469
4	**4c'**	Me	Ph	Ph	Ph	*RR*/*SS*-overlapped	484
5	**5p**[c]	Me	4Br-Ph	4Br-Ph	Ph	*RS*-paired	425
6	**5b**	Me	4Br-Ph	4Br-Ph	Ph	*RR*/*SS*-paired	445
7	**5c**	Me	4Br-Ph	4Br-Ph	Ph	*RR*/*SS*-overlapped	468
8	**6c**	Me	Ph	Ph	4Br-Ph	*RS*-overlapped	459
9	**6c'**	Me	Ph	Ph	4Br-Ph	*RR*/*SS*-overlapped	488
10	**7c**	Me	4F-Ph	4F-Ph	Ph	*RS*-paired	465
11	**7c'**	Me	4F-Ph	4F-Ph	Ph	*RR*/*SS*-overlapped	486

[a] Molecular packing modes. [b] Maximum emission wavelength. [c] purple fluorescence.

5. The photos of the as-synthesized 1b, 1c, 2, 3 and their corresponding ground powder taken under natural light

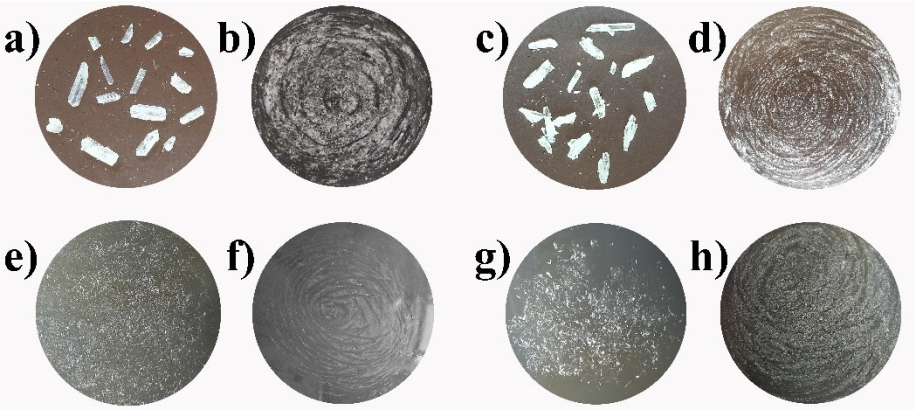


Fig. S1 The photos of the as-synthesized (a) **1b**, (c) **1c**, (e) **2**, (g) **3** and their corresponding ground powder of (b) **1b**, (d) **1c**, (f) **2** and (h) **3** taken under natural light.

6. The absorption spectra of the as-synthesized 1b, 1c, 2, 3 and their corresponding ground powder and fumed solids

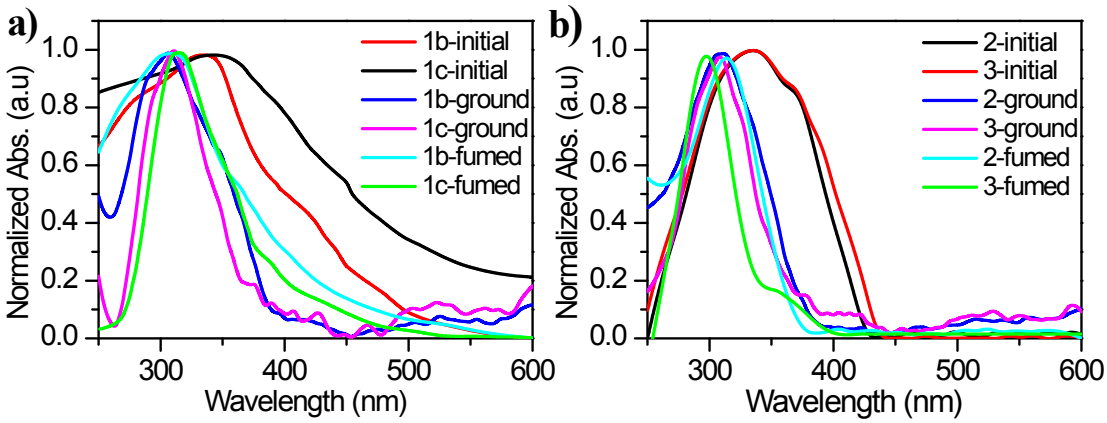


Fig. S2 The absorption spectra of the as-synthesized (a) **1b**, **1c**, (b) **2**, **3** and their corresponding ground powder and fumed solids.

7. The Fluorescence decay profiles of the as-synthesized 2, 3 and the ground powder of 1b, 1c, 2 and 3

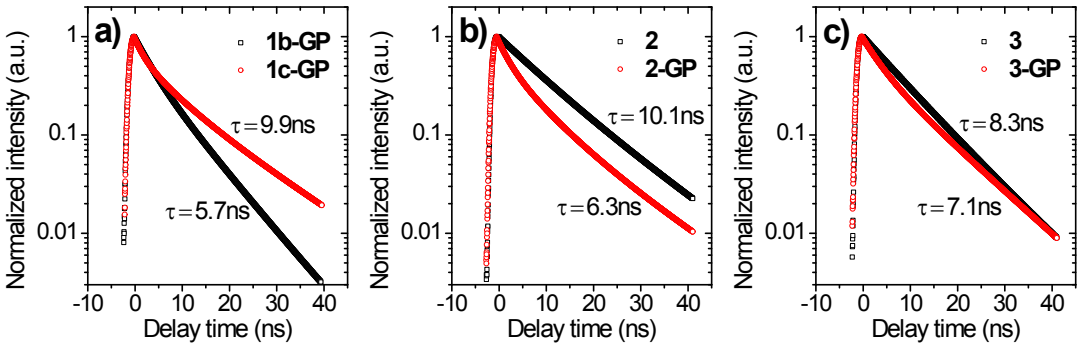


Fig. S3 Fluorescence decay profiles of (a) the ground powder (indicated as GP) of **1b** and **1c**, (b) the as-synthesized **2** and its ground powder, and (c) the as-synthesized **3** and its ground powder. Excited at 360 nm.

8. Calculated HOMOs and LUMOs of THPs 1-3

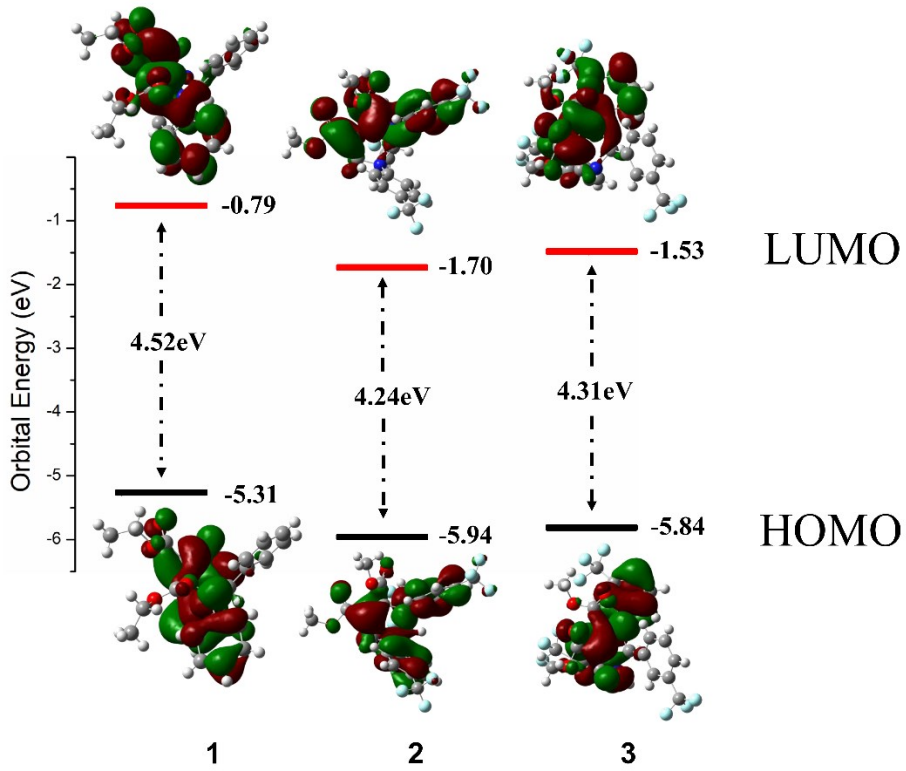


Fig. S4 Calculated HOMOs and LUMOs of THPs **1-3** using DFT/B3LYP/6-31G method.

9. The ^{1}HNMR and ^{13}CNMR spectra of THP 1-3

Listed below are the ^{1}HNMR and ^{13}CNMR spectra of THP **2**, and the ^{1}HNMR spectra of THP **1** and **3**, which are the same as we reported previously.[1,2]

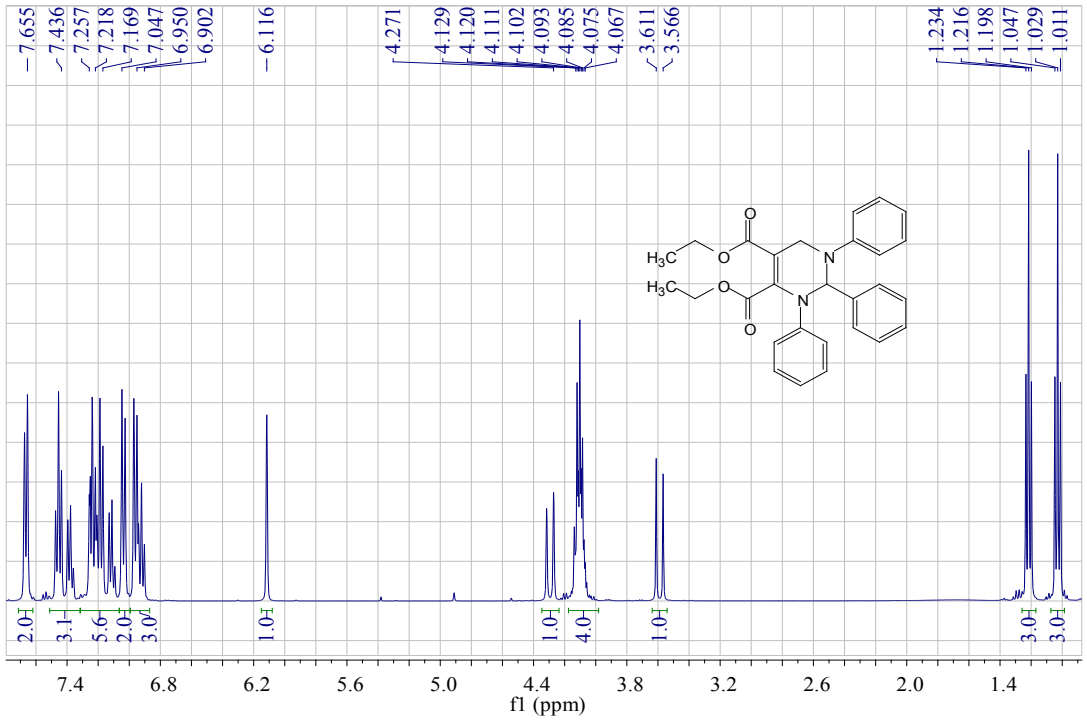


Fig. S5 The [1]HNMR spectrum of THP **1**.

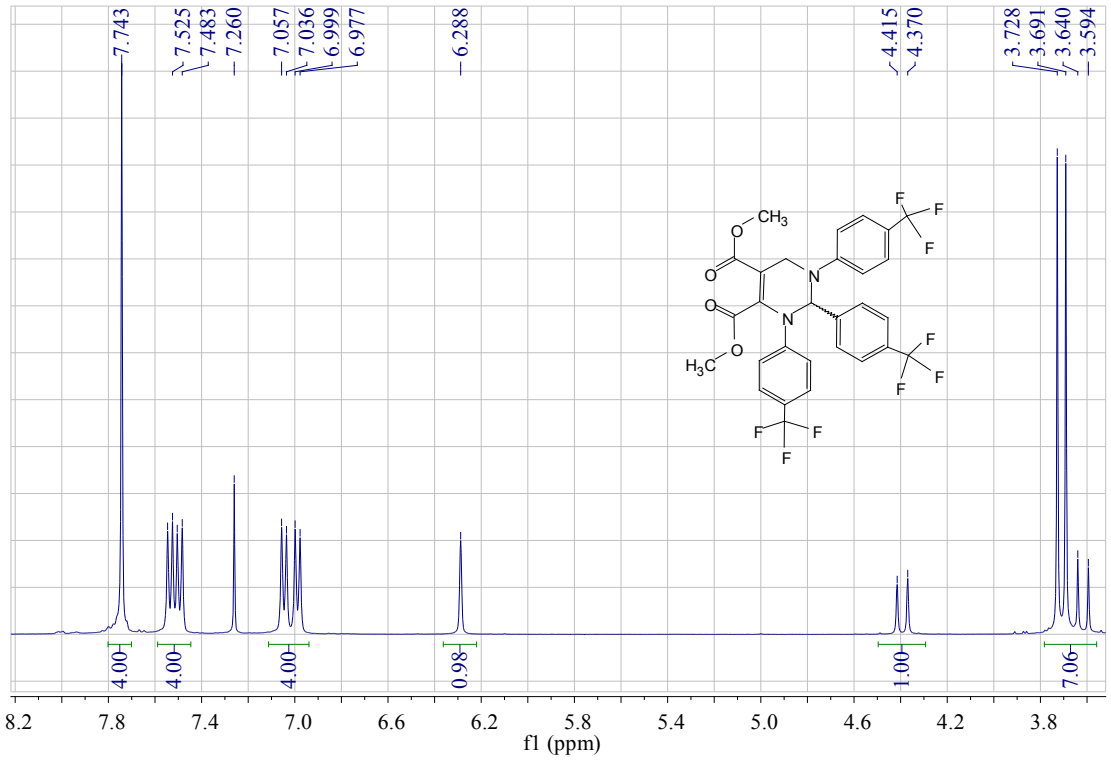


Fig. S6 The [1]HNMR spectrum of THP **2**.

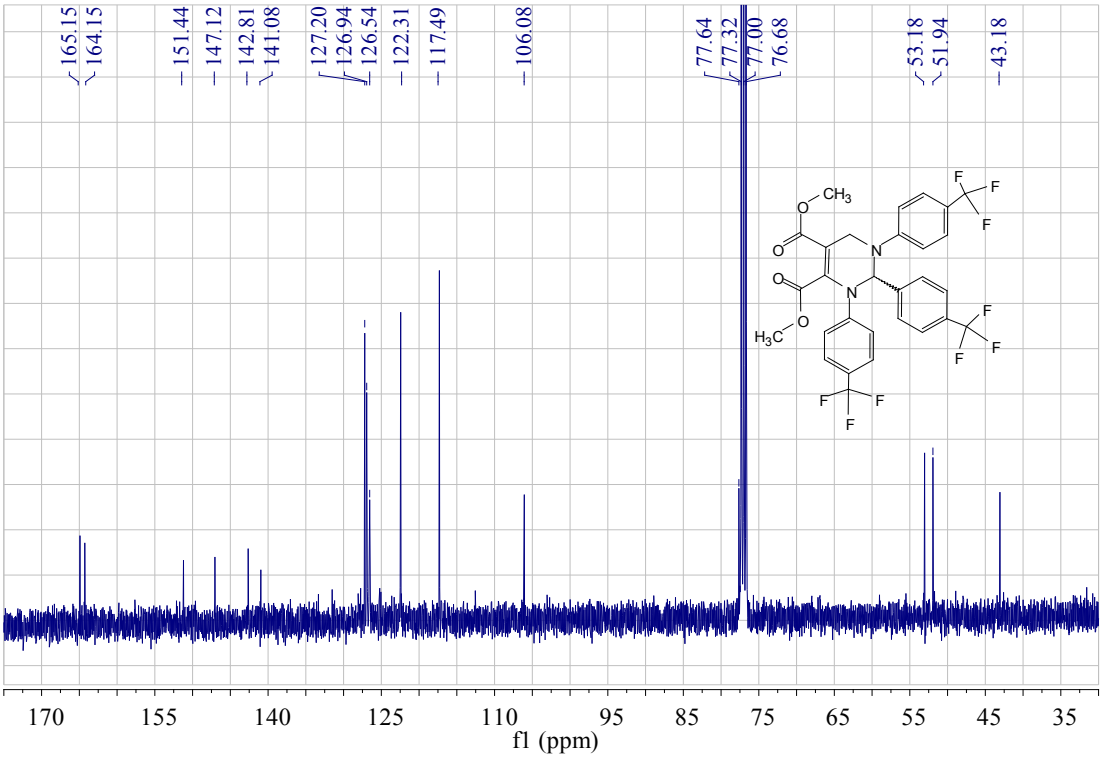


Fig. S7 The ^{13}CNMR spectrum of THP **2**.

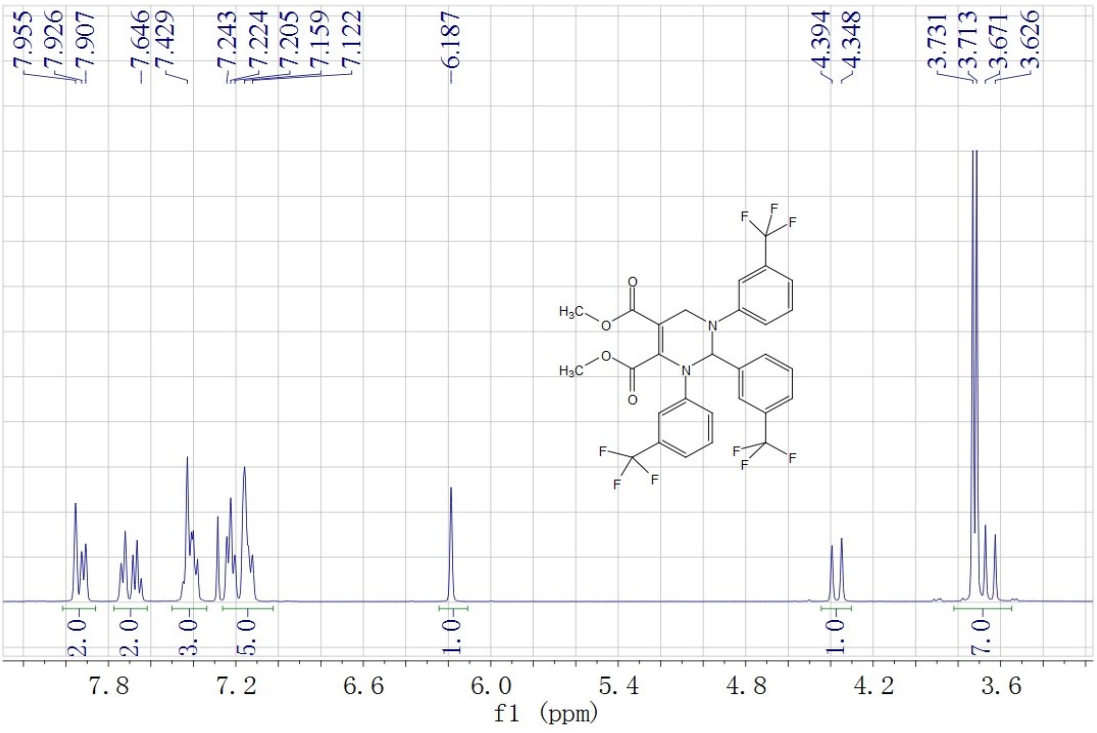


Fig. S8 The ^{1}HNMR spectrum of THP **3**.

References

1 Q. Zhu, L. Huang, Z. Chen, S. Zheng, L. Lv, Z. Zhu, D. Cao, H. Jiang and S. Liu, *Chem. Eur. J.*, 2013, **19**, 1268-1280.

2 Q. Zhu, S. Wu, S. Zheng, Z. Ye, C. Huang and Y. Liu, *Dyes Pigments*, 2019, **162**, 543-551.