

## Supplementary Material

### Exploring the use of anionic homoleptic complexes as templates in the design of photoreactive multi-component supramolecular assemblies.

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**Figure S10.** (a) Photographs of powder sample of **1** under room light and UV(302 nm) (from left to right). (b) Powder and single crystals of **2** under room light and UV(302 nm). (c) Photographs of powder sample of **3** under room light and UV(302 nm)

## 1. Experimental Section

All reagents were obtained from commercial sources and used without further purification. The elemental analyses were performed (C, H, N) on a model EA1108 Fisons elemental analyzer. The FT-IR spectra were recorded from KBr discs, using a Nicolet Magna-IR 560 spectrophotometer. XRPD patterns were recorded on a Siemens D5005 Diffractometer with Cu(K $\alpha$ ) (1.5418 Å) radiation, with a scan speed of 2 deg/min. These patterns showed that compounds **1-3** and **5-7** were obtained as pure single-phases (Figs. S1-S6). The  $^1\text{H}$  NMR spectra of the isolated products were recorded on a Bruker AVANCE-300 Spectrometer in  $\text{CDCl}_3$ .

**Crystal structure determination.** Intensity data were recorded at room temperature on a Rigaku AFC-7S diffractometer equipped with a Mercury CCD bidimensional detector using monochromated Mo(K $\alpha$ ) radiation ( $\lambda = 0.71073$  Å). An empirical absorption correction (multi-scan) was applied using the package CrystalClear. The structures were solved by Direct Methods and refined by full-matrix least-squares on  $F^2$  using the SHELXTL-PLUS package. Hydrogen atoms were placed at fixed positions using the HFIX instruction. H-atoms on coordinated water and/or methanol molecules were found from the Difference Fourier map. They were refined with isotropic displacement parameters set to  $1.2 \times U_{eq}$  of the attached atom. The non-hydrogen atoms of these molecules were refined with isotropic displacement parameters. In structure of **2**, (2,2'-H<sub>2</sub>bpe)<sup>2+</sup> cation was found to be disordered and was modelled in two sets of positions and constraining the pyridyl rings to be regular hexagons. The occupational parameters were determined to be 50:40. Likewise, in structure of **4**, both (4,4'-Hbpe)<sup>+</sup> cations were found to be disordered and were also modelled in two sets of positions with occupational parameters 53:47 and 58:42, respectively

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre with the following deposition numbers CCDC -----

**Synthesis of (2,2'-H<sub>2</sub>bpe)<sub>0.5</sub>(2,2'-Hbpe)[Zn(NCS)<sub>4</sub>]·2(H<sub>2</sub>O) (**1**).** A mixture of ZnCl<sub>2</sub> (77 mg, 0.5 mmol), NaSCN (188 mg, 2 mmol) and 2,2'-bpe (105 mg, 0.5 mmol) in a molar ratio of 1:4:1 were dissolved using a mixture of H<sub>2</sub>O/Methanol 50:50. The pH of the solution was adjusted at 5 by addition of a HCl diluted solution. Yield 78% (pale brown crystals). Anal. calcd. (%) for C<sub>22</sub>H<sub>20</sub>N<sub>7</sub>O<sub>2</sub>S<sub>4</sub>Zn: C, 43.45; H, 3.32; N, 16.13; S,

21.09. Found: C, 43.46; H, 3.55; N, 15.84; S, 21.10. IR (cm<sup>-1</sup>):  $\nu$ (N-H): 3419,  $\nu$ (NCS): 2083,  $\nu$ (C-C): 1614,  $\nu$ (C-N): 1466.

**Synthesis of (2,2'-H<sub>2</sub>bpe)[Zn(NCS)<sub>4</sub>]·2(H<sub>2</sub>O) (2).** A mixture of ZnCl<sub>2</sub> (77 mg, 0.5 mmol), NaSCN (180 mg, 2 mmol) and 2,2'-bpe (105 mg, 0.5 mmol) in a molar ratio of 1:4:1 were dissolved using a mixture of H<sub>2</sub>O/Methanol 50:50. The pH of the solution was adjusted at 3 by addition of HCl. Yield 75% (yellow crystals). Anal. calcd. (%) for C<sub>16</sub>H<sub>14</sub>N<sub>6</sub>S<sub>4</sub>Zn: C, 38.44; H, 2.82; N, 16.81; S, 25.65. Found: C, 37.11; H, 3.05; N, 16.19; S, 25.18. IR (cm<sup>-1</sup>):  $\nu$ (N-H): 3425,  $\nu$ (NCS): 2083,  $\nu$ (C-C): 1613,  $\nu$ (C-N): 1466.

**Synthesis of (4,4'-H<sub>2</sub>bpe)[Zn(NCS)<sub>4</sub>] (3).** A mixture of ZnCl<sub>2</sub> (77 mg, 0.5 mmol), NaSCN (180 mg, 2 mmol) and 4,4'-bpe (105 mg, 0.5 mmol) in a molar ratio of 1:4:1 were dissolved using a mixture of H<sub>2</sub>O/Methanol 50:50. The pH of the solution was adjusted at 3 by addition of HCl. Yield 69% (yellow crystals). Anal. calcd. (%) for C<sub>16</sub>H<sub>12</sub>N<sub>6</sub>S<sub>4</sub>Zn: C, 38.44; H, 2.82; N, 16.81; S, 25.65. Found: C, 38.07; H, 2.95; N, 16.05; S, 25.18. IR (cm<sup>-1</sup>):  $\nu$ (N-H): 3420,  $\nu$ (NCS): 2080,  $\nu$ (C-C): 1610,  $\nu$ (C-N): 1463.

**Synthesis of (2,2'-Hbpe)<sub>4</sub>[Fe(NCS)<sub>6</sub>]·4H<sub>2</sub>O (4).** A mixture of FeSO<sub>4</sub>·7H<sub>2</sub>O (64 mg, 0.2 mmol), NaSCN (115 mg, 1 mmol) and 2,2'-bpe (102 mg, 0.5 mmol) in a molar ratio of 1:2:2 was dissolved using a mixture of H<sub>2</sub>O/Ethanol 50:50. Slow evaporation of the resulting solutions at room temperature gave a mixture of crystals. The major phase was unsuccessfully characterised by X ray-single crystal analysis (yellow plates). The minor phase obtained with a yield (based on 2,2'-bpe) of 8% yield (purple crystals). Anal. calcd. (%) for C<sub>54</sub>H<sub>52</sub>FeN<sub>14</sub>O<sub>4</sub>S<sub>6</sub>: C, 53.63; H, 4.33; N, 16.22; S, 15.90. Found: C, 53.99; H, 4.20; N, 14.82; S, 11.16.

**Synthesis of (4-HStb)<sub>2</sub>[Zn(NCS)<sub>4</sub>] (5).** A mixture of ZnCl<sub>2</sub> (44 mg, 0.3 mmol), NaSCN (124 mg, 2 mmol) and *trans*-1-(4pyridyl)-2-(phenyl)ethylene (4-Stb) (200 mg, 0.9 mmol) in a molar ratio of 1:2:4 was dissolved using a mixture of H<sub>2</sub>O/Methanol 50:50. The pH of the solution was adjusted at 3-2 by addition of HCl. Yield 71% (yellow crystals). Anal. calcd. (%) for C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>S<sub>4</sub>Zn: C, 54.42; H, 3.65; N, 12.69; S, 19.37.

Found: C, 55.23; H, 3.76; N, 12.49; S, 19.24. IR (cm<sup>-1</sup>):  $\nu$ (N-H): 3412,  $\nu$ (NCS): 2081,  $\nu$ (C-C): 1621-1589,  $\nu$ (C-N): 1500.

**Synthesis of (4-HStb)<sub>2</sub>[Co(NCS)<sub>4</sub>] (6).** A mixture of CoCl<sub>2</sub>·6H<sub>2</sub>O (44 mg, 0.3 mmol), NaSCN (124 mg, 2 mmol) and *trans*-1-(4pyridyl)-2-(phenyl)ethylene (4-Stb) (200 mg, 0.9 mmol) in a molar ratio of 1:2:4 was dissolved using a mixture of H<sub>2</sub>O/Methanol 50:50. The pH of the solution was adjusted at 3 by addition of HCl. Yield 63% (dark blue crystals). Anal. calcd. (%) for C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>S<sub>4</sub>Co: C, 54.95; H, 3.69; N, 12.82; S, 19.56. Found: C, 56.51; H, 3.73; N, 12.16; S, 19.11. IR (cm<sup>-1</sup>):  $\nu$ (N-H): 3415,  $\nu$ (NCS): 2072,  $\nu$ (C-C): 1619-1586,  $\nu$ (C-N): 1503.

**Synthesis of (4-HStb)<sub>2</sub>[ZnCl<sub>4</sub>] (7).** A mixture of ZnCl<sub>2</sub> (22 mg, 0.15 mmol), and *trans*-1-(4pyridyl)-2-(phenyl)ethylene (4-ST) (53 mg, 0.3 mmol) in a molar ratio 1:2 was dissolved using a mixture of H<sub>2</sub>O/Methanol 50:50. The pH of the solution was adjusted at 3 by addition of HCl. Yield 58% (yellow crystals). Anal. calcd. (%) for C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>Cl<sub>4</sub>Zn: C, 54.63; H, 4.23; N, 4.90. Found: C, 55.11; H, 4.08; N, 5.01; IR (cm<sup>-1</sup>):  $\nu$ (N-H): 3415,  $\nu$ (C-C): 1618,  $\nu$ (C-N): 1451.

### Solid state reactivity.

A powdered crystalline sample of each of the compounds (100 mg) was irradiated with a 100 Watt Hg lamp at 354 nm during 2-3 days. The products were isolated from an extraction with CH<sub>2</sub>Cl<sub>2</sub> after the neutralization of the compounds with NaOH in either case

<sup>1</sup>H NMR data for dimers obtained from **1** and **2** irradiated:

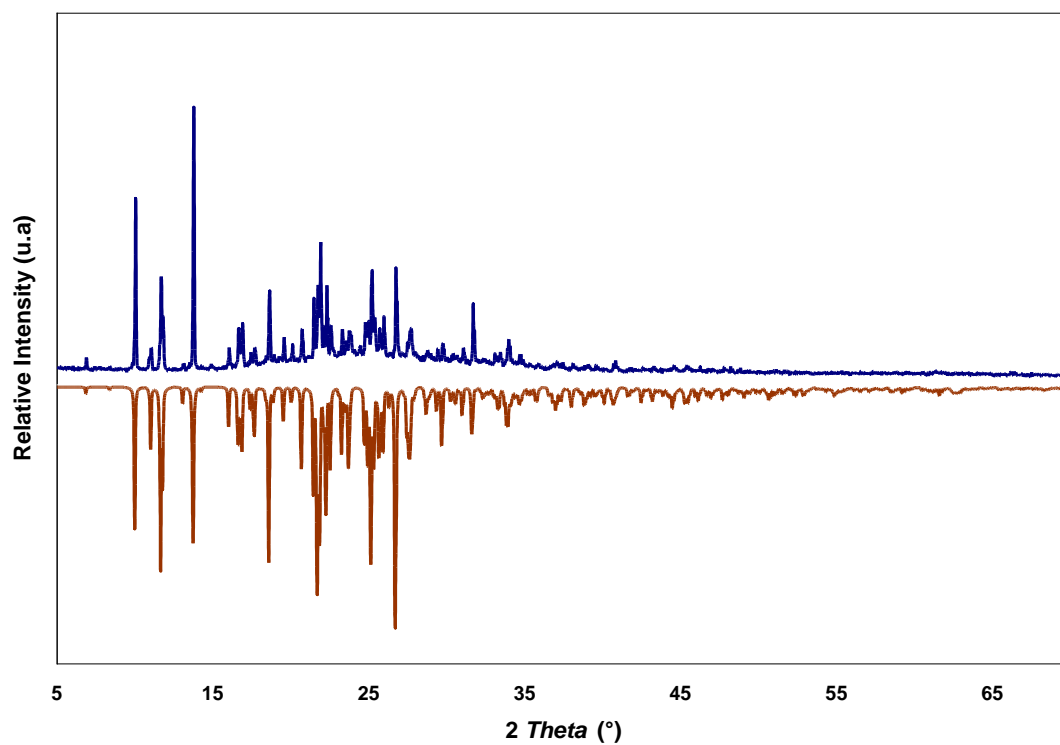
**Dimer of 2,2'-bpe: [*rctt*-tetrakis(2-pyridyl)cyclobutane isomer (*rctt*-2,2'-tpcb)]** was obtained by topochemical reaction from compounds **1** and **2**. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$ <sub>H</sub>(ppm), *J* (Hz): 8.35(H<sub>a</sub>, ddd, *J*<sub>ab</sub>: 4.9; *J*<sub>ac</sub>: 1.8; *J*<sub>ad</sub>: 0.9), 7.33(H<sub>c</sub>, ddd, *J*<sub>bc</sub>: 7.7), 7.03(H<sub>d</sub>, d), 6.88 (H<sub>b</sub>, m) and 5.04(H<sub>e</sub>, s).

<sup>1</sup>H NMR data for dimers obtained from **5**, **6** and **7** irradiated:

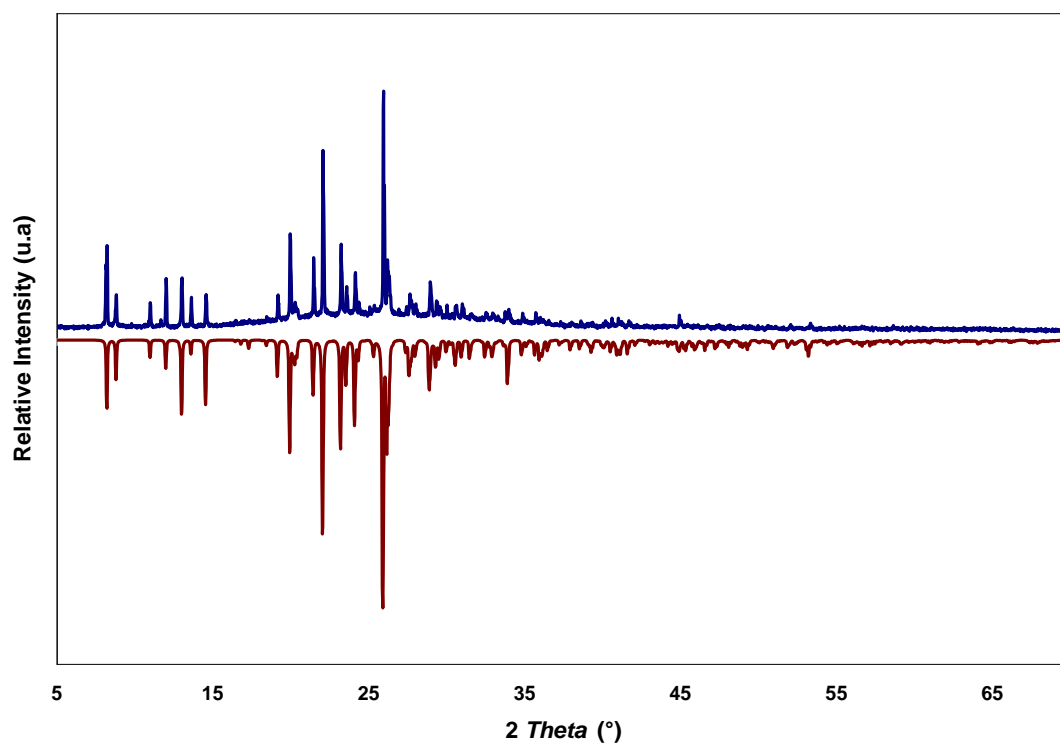
**Dimer of 4-Stb: [*rctt*-1,3-bis(4-pyridyl)-2,4-bis(phenyl)cyclobutane]**

(300 MHz, CDCl<sub>3</sub>),  $\delta$ <sub>H</sub>(ppm): 8.34(4H<sub>a</sub>, d), 7.03-7.4(14H<sub>b-d</sub>, m), and 4.45(4H<sub>e-f</sub>, m).

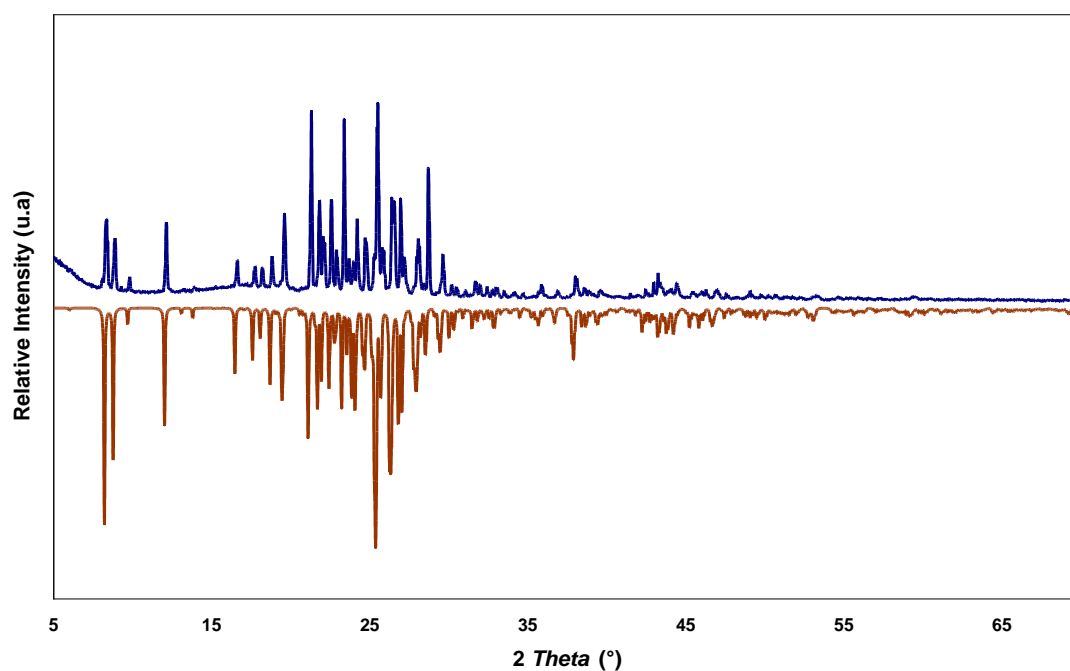
**Figure S1.** The simulated (red) and experimental (blue) XRD patterns for compound **1**



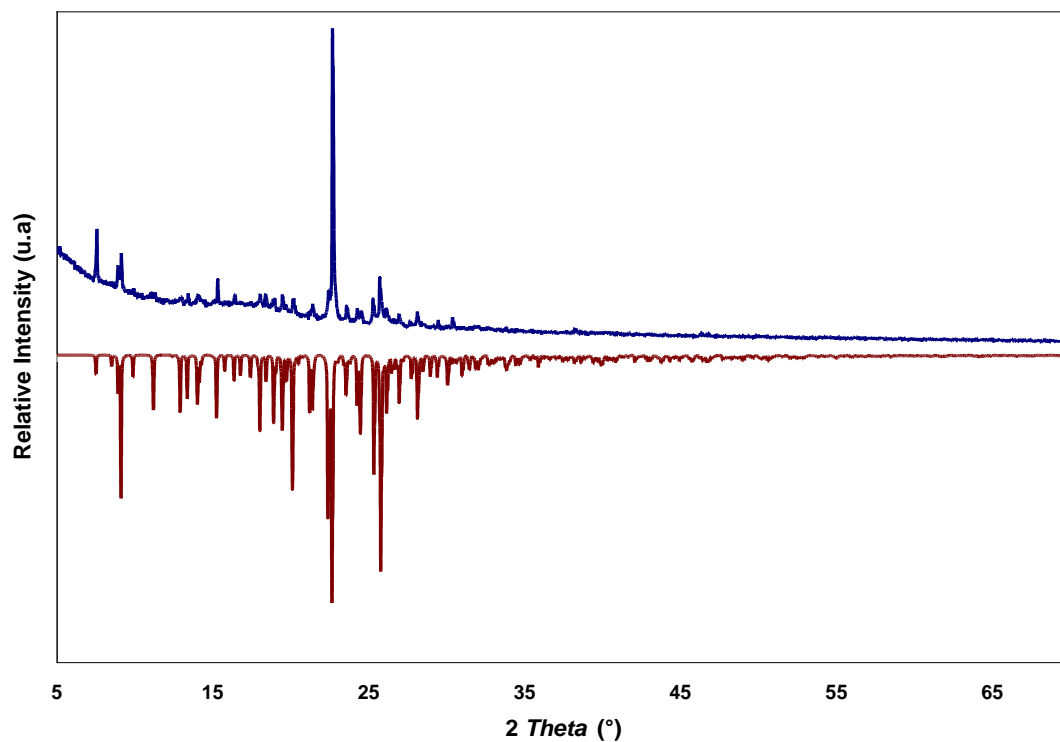
**Figure S2.** The simulated (red) and experimental (blue) XRD patterns for compound **2**



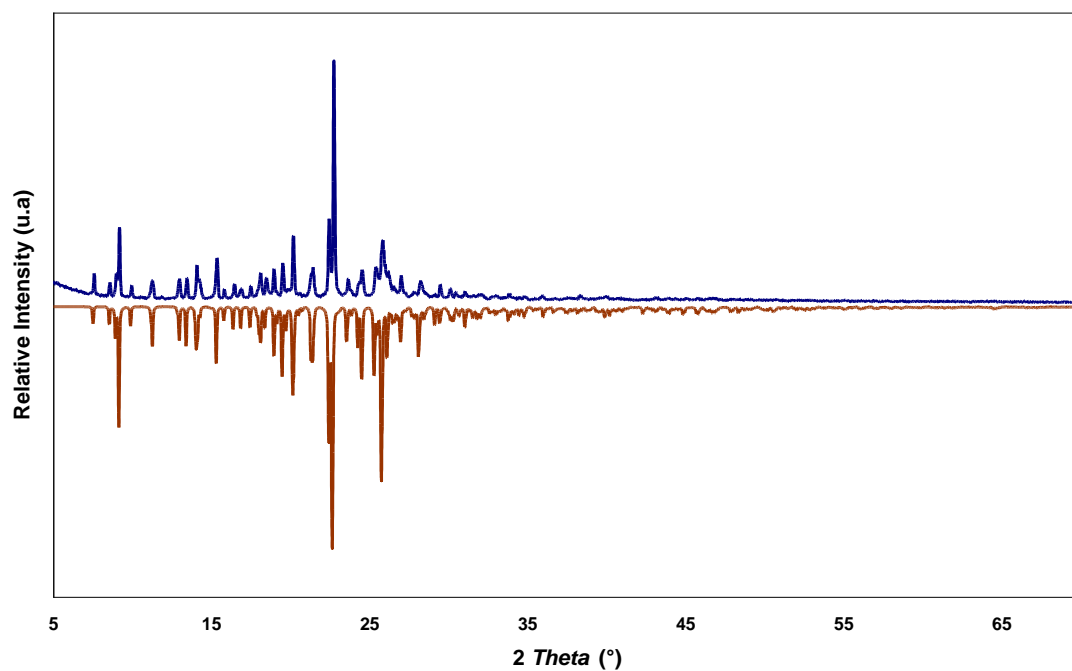
**Figure S3.** The simulated (red) and experimental (blue) XRD patterns for compound **3**.



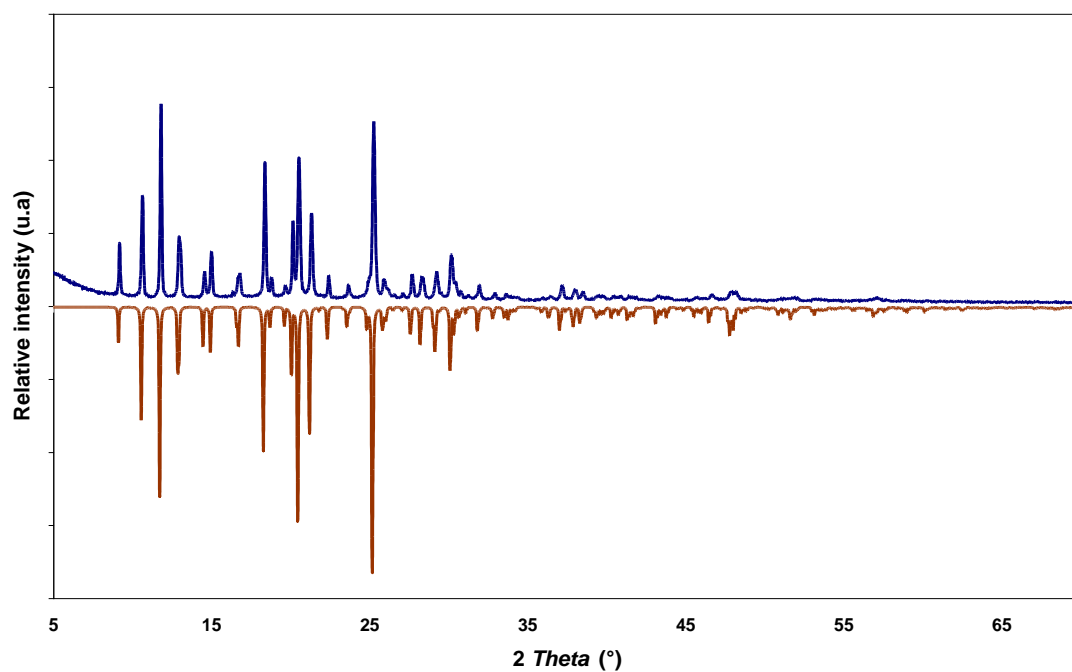
**Figure S4.** The simulated (red) and experimental (blue) XRD patterns for compound **5**. This pattern is affected either by preferred orientation or by excitation of Co fluorescence.



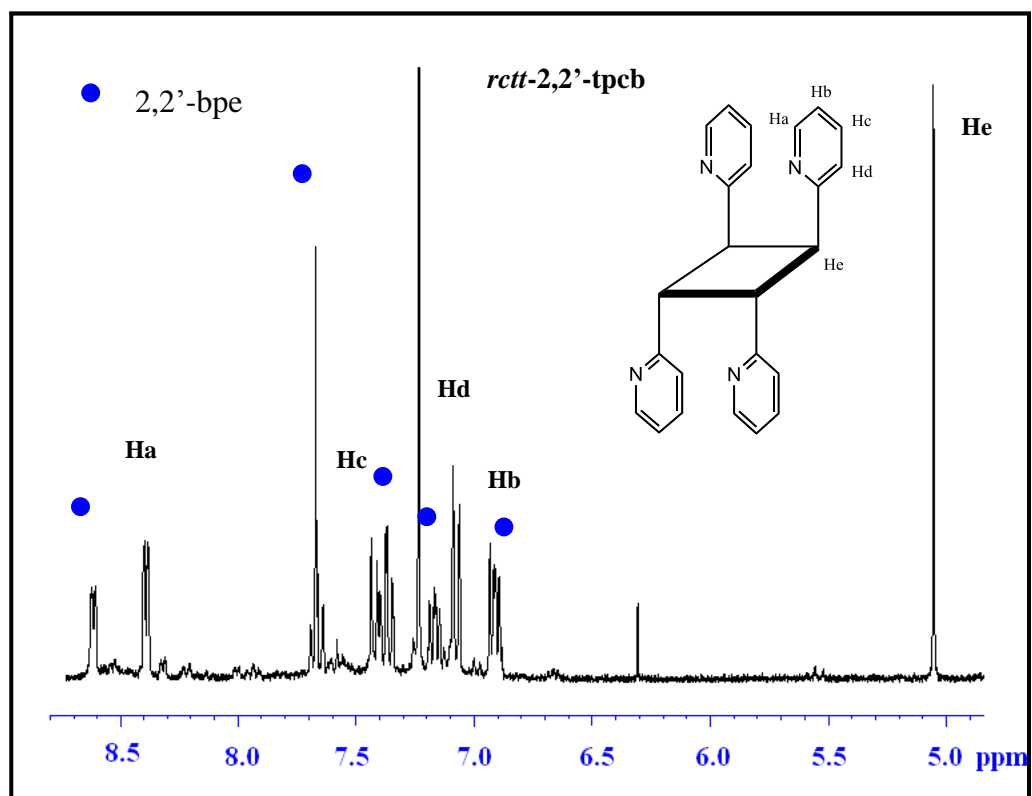
**Figure S5.** The simulated (red) and experimental (blue) XRD patterns for compound **6**.



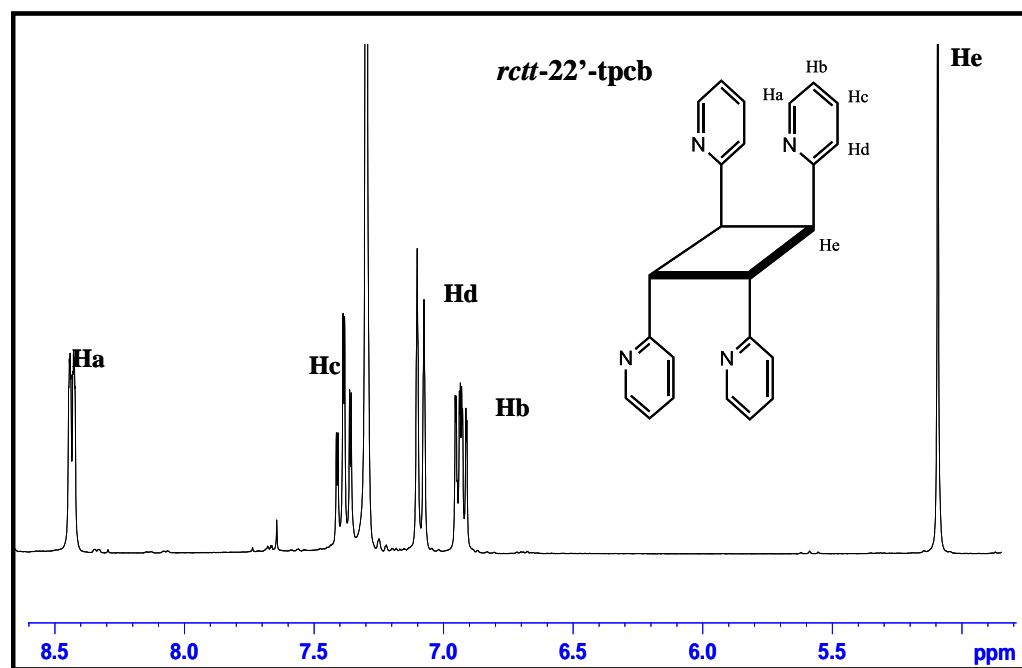
**Figure S6.** The simulated (red) and experimental (blue) XRD patterns for compound **7**.



**Figure S7.**  $^1\text{H}$  NMR spectrum of the *rctt*-2,2'-tpcb isomer obtained from the photoreaction of compounds **1** (a) and **2** (b).



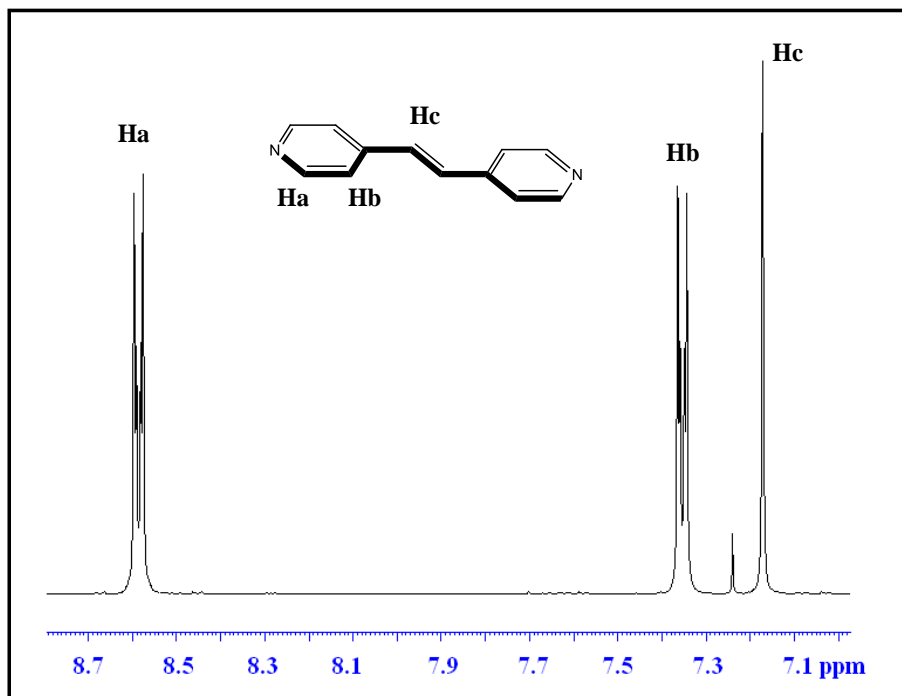
(a)



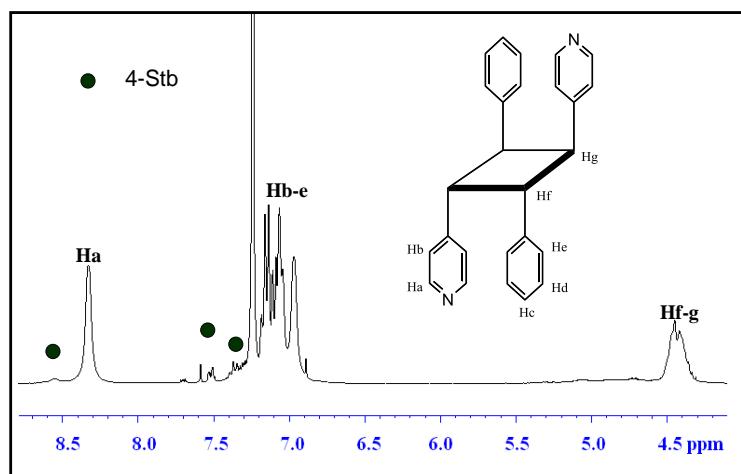
(b)



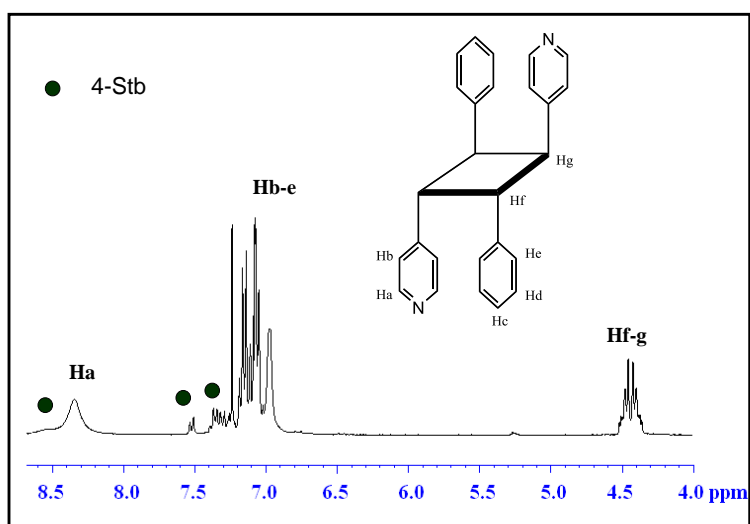
**Figure S8.**  $^1\text{H}$  NMR spectrum of 4,4'-bpe after the irradiation of compound **3**.



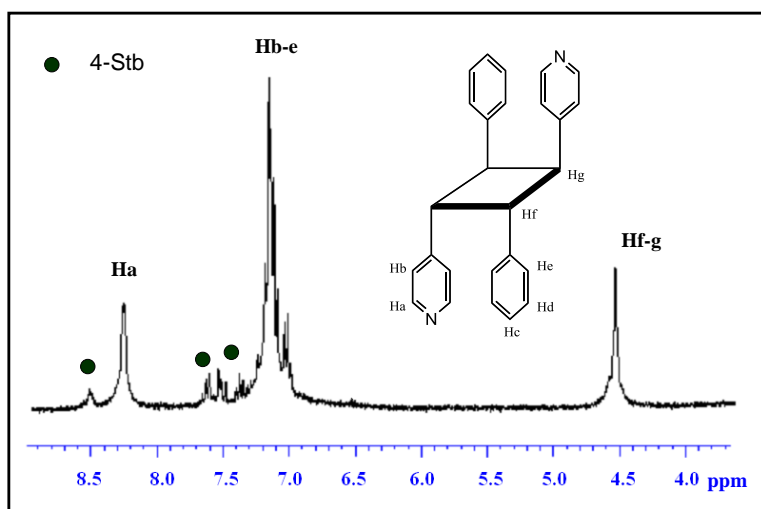
**Figure S9.** (a)  $^1\text{H}$  NMR spectrum of the ht-isomer: (*rc*tt-1,3-bis(4-pyridyl)-2,4-bis(phenyl)cyclobutane) obtained from the photoreaction of compounds **5** (a) **6** (b) and **7**(c).



(a)

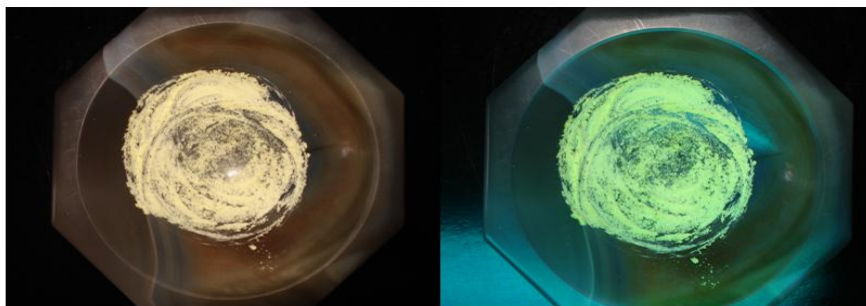


(b)

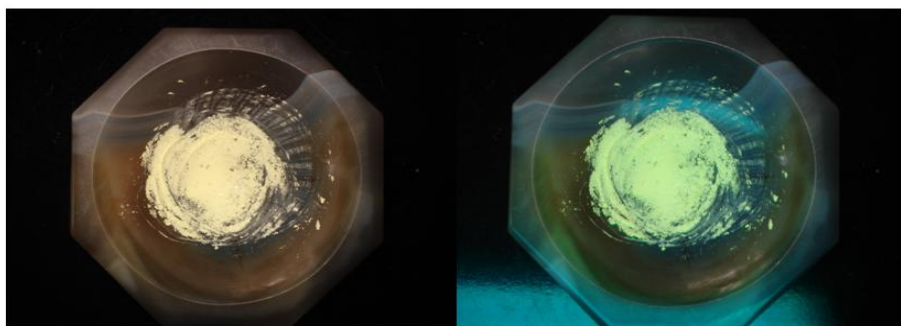


(c)

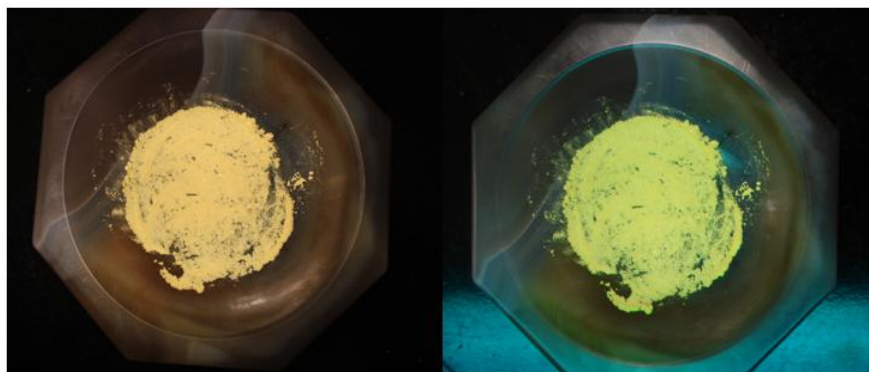
**Figure S10.** (a) Photographs of powder sample of **1** under room light and UV(302 nm) (from left to right). (b) Powder and single crystals of **2** under room light and UV(302 nm). (c) Photographs of powder sample of **3** under room light and UV(302 nm)



(a)



(b)



(c)