

Supplementary Material

Solid state synthesis of head-to-tail photodimers from supramolecular assemblies directed by charge assisted hydrogen bonds

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Figure S5. ^1H NMR spectrum of irradiated sample of $(\text{bta}^{2-})\cdot 2(4\text{-OH-HStb}^+)$ (**4**).

1. Experimental Section

All reagents were obtained from commercial sources and used without further purification. The elemental analysis was 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. The ^1H NMR spectra were recorded on a Bruker AVANCE-300 Spectrometer in CDCl_3 or DMSO.

Crystals of **1-4** were prepared by mixing of 1,2,4,5 benzenetetracarboxylic acid (**bta**) and each pyridyl compounds, respectively in 1:2 molar ratio in MeOH/DMSO solution. Slow evaporation of the resulting solutions at room temperature gave crystals of good quality for X-ray single crystal analysis. Compound (**bta** $^{2-}$) \cdot 2(**3,4-Hbpe** $^+$) (**1**); [3,4-bpe: *trans*-1-(3-pyridyl)-2-(4-pyridyl)ethylene] Yield: 85% (brown prisms). Anal. calcd. (%) for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_4$: C, 66.01; H, 4.24; N, 9.06. Found: C, 65.28; H, 4.22; N, 9.15. IR (cm^{-1}): $\nu(\text{C-H})$: 3066, $\nu(\text{C=O})$: 1698, $\nu(\text{C=C, C=N})$: 1500-1451, $\nu_{\text{asim}}(\text{CO}_2^-)$: 1633, $\nu_{\text{sim}}(\text{CO}_2^-)$: 1340 $\nu(\text{C-H})$: 991. (**bta** $^{2-}$) \cdot 2(**4-HStb** $^+$) (**2**). yield 88% (Colourless prisms). Anal. calcd. (%) for $\text{C}_{18}\text{H}_{14}\text{NO}_4$: C, 70.13; H, 4.58; N, 4.54. Found: C, 70.33; H, 4.45; N, 4.50. IR (cm^{-1}): $\nu(\text{N-H})$: 3420, $\nu(\text{C-H})$: 3061, $\nu(\text{C=O})$: 1691, $\nu(\text{C=C, C=N})$: 1558-1452, $\nu_{\text{asim}}(\text{CO}_2^-)$: 1635, $\nu_{\text{sim}}(\text{CO}_2^-)$: 1341, $\nu(\text{C-H})$: 973.

(**bta** $^{2-}$) \cdot 2(**4-Cl-HStb** $^+$) (**3**), yield 73% (pale yellow prisms). Anal. calcd. (%) for $\text{C}_{18}\text{H}_{13}\text{ClNO}_4$: C, 63.07; H, 3.82; N, 4.07. Found: C, 62.82; H, 3.75; N, 4.12. IR (cm^{-1}): $\nu(\text{O-H})$: 3420, $\nu(\text{C=O})$: 1695, $\nu(\text{C=C, C=N})$: 1565-1491, $\nu_{\text{asim}}(\text{CO}_2^-)$: 1625, $\nu_{\text{sim}}(\text{CO}_2^-)$: 1342, $\nu(\text{C-Cl})$: 1084.

(**bta** $^{2-}$) \cdot 2(**4-OH-HStb** $^+$) (**4**) yield 69% (yellow prisms). Anal. calcd. (%) for $\text{C}_{18}\text{H}_{14}\text{NO}_5$: C, 66.67; H, 4.35; N, 4.32. Found: C, 67.02; H, 4.28; N, 4.45. IR (cm^{-1}): $\nu(\text{O-H})$: 3600-3100, $\nu(\text{C=O})$: 1626, $\nu(\text{C=C, C=N})$: 1515-1435, $\nu_{\text{asim}}(\text{CO}_2^-)$: 1598-1581, $\nu_{\text{sim}}(\text{CO}_2^-)$: 1355, $\nu(\text{C-H})$: 975.

Crystals of **5** were obtained from slow evaporation of a diluted solution of a mixture of bta and 4-Cl-Stb then of 4-5 weeks or recrystallisation of **3** in DMSO/methanol, after irradiated with UV-light in the solid state: (**bta** $^{2-}$) \cdot (4-Cl-dpcb $^{2+}$) \cdot 2DMSO (**5**) (colourless prisms). Anal. calcd. (%) for $\text{C}_{40}\text{H}_{38}\text{Cl}_2\text{N}_2\text{O}_{10}\text{S}_2$: C, 57.08; H, 4.55; N, 3.33; S, 7.60. Found: C, 57.23; H, 4.41; N, 3.44; S, 7.30. IR (cm^{-1}): $\nu(\text{O-H})$: 3600-3100, $\nu(\text{C=O})$: 1713, $\nu(\text{C=C, C=N})$: 1490-1412, $\nu_{\text{asim}}(\text{CO}_2^-)$: 1624-1581, $\nu_{\text{sim}}(\text{CO}_2^-)$: 1363, $\nu(\text{C-Cl})$: 1006.

Solid state reactivity.

The reactivity of compounds **1-4** was studied upon irradiation with a UV light. A powdered crystalline (50 mg) and crystals of **1-4** were irradiated at 354 nm for 2 days. The irradiated samples were characterised by ¹H NMR spectroscopy for monitoring the respective topochemical transformations. The dimers were obtained by reaction from the compounds **1**, **2** and **3** in high yield (82-100%). These compounds were isolated from an extraction with CH₂Cl₂ after the neutralization of the component acid with NaOH in either case, except for **3**. ¹H NMR data for dimers obtained from **2** and **3** irradiated

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

(300 MHz, CDCl₃), δ_{H} (ppm), *J* (Hz): 8.34(4H, d), 7.03-7.4(14H, m), and 4.45(4H, m).

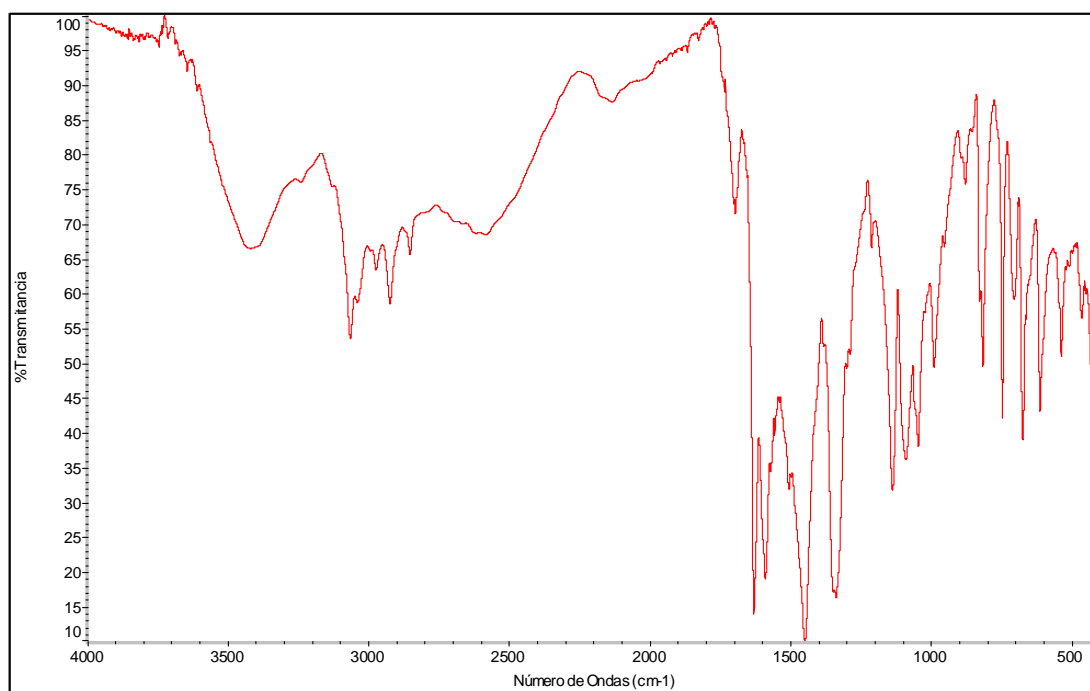
Dimer of 4-Cl-Stb: [*rctt*-1,3-bis(4-pyridyl)-2,4-bis(4-chlorophenyl)cyclobutane]

(300 MHz, DMSO), δ_{H} (ppm), *J* (Hz): 8.38(4H, d), 8.02(2H, s, template (bta)), 7.27(4H, d) 7.21(8H, s), and 4.57(4H, m).

Crystal structure determination. Intensity data were recorded at room temperature on a Rigaku AFC-7S diffractometer equipped with a CCD bidimensional detector using monochromated Mo(K α) radiation ($\lambda = 0.71073 \text{ \AA}$). An empirical absorption correction (multi-scan) was applied using the package CrystalClear.²⁰ The structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL-PLUS package.²¹ Hydrogen atoms on the carbon atoms were placed at fixed positions using the HFIX instruction. H-atoms on carboxylic groups and pyridyl rings were found from the Difference Fourier map. They were refined with isotropic displacement parameters set to $1.2 \times U_{\text{eq}}$ of the attached atom. In structure of **1**, (3,4-Hbpe)⁺ 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 55:45.

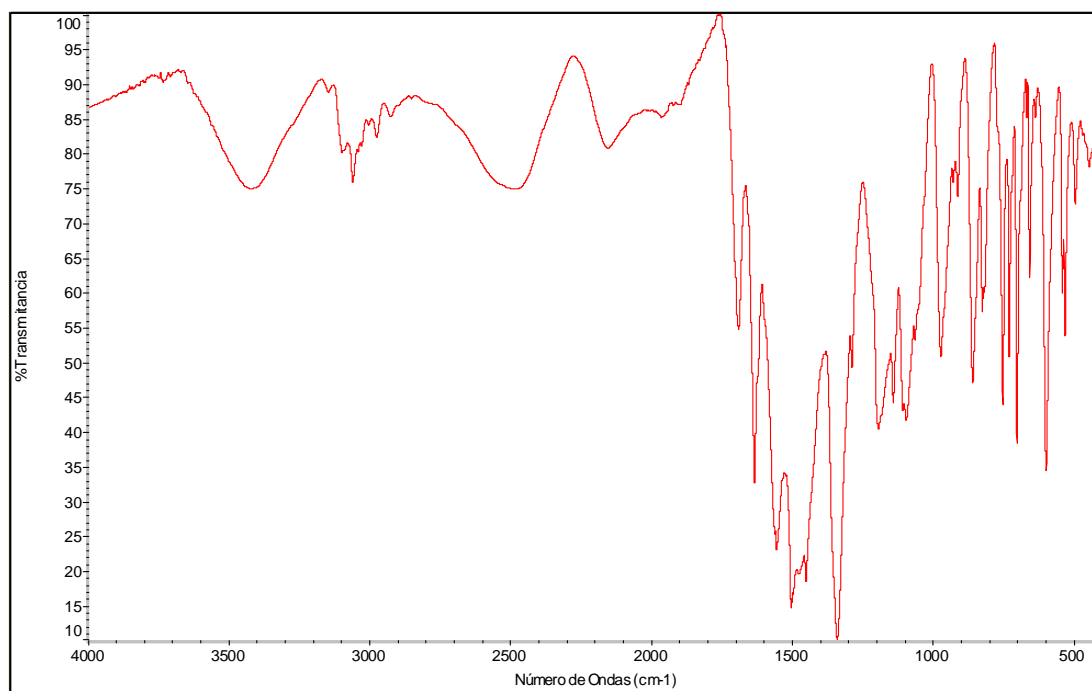
Figure S1. FT-IR spectra of compounds **1-4** in KBr disk (a-d).

(a) FT-IR spectrum of $(\text{bta}^{2-}) \cdot 2(3,4\text{-Hbpe}^+)$ (**1**)

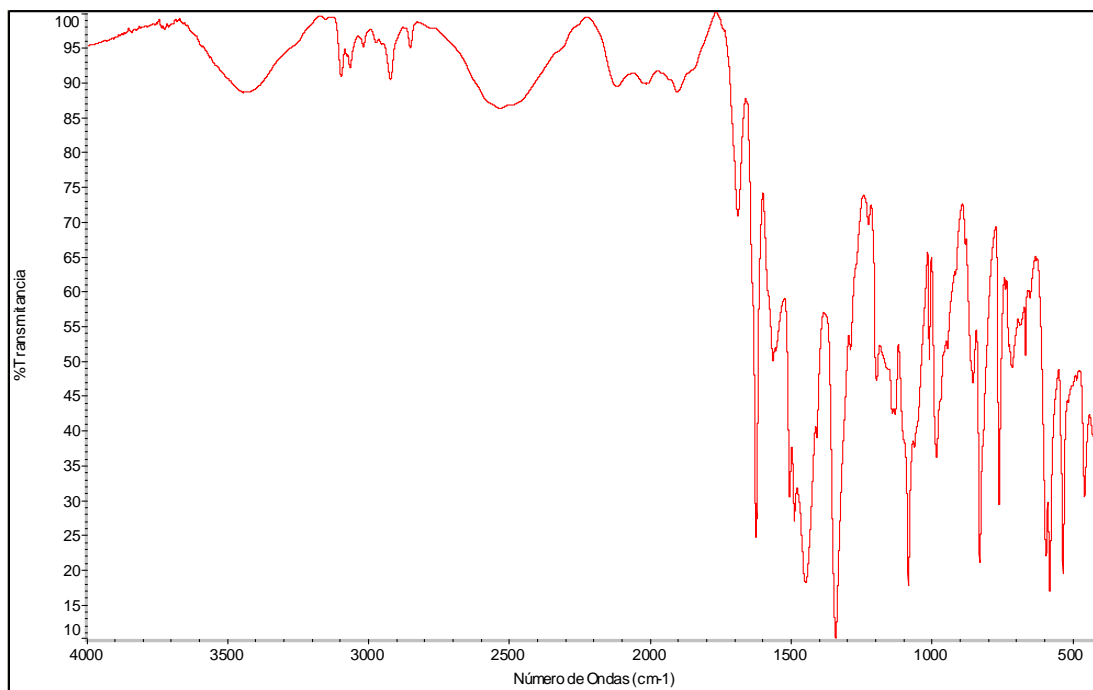


(a)

(b) FT-IR spectrum of $(\text{bta}^{2-}) \cdot 2(4\text{-HStb}^+)$ (**2**).



(c) FT-IR spectrum of $(\text{bta}^{2-}) \cdot 2(4\text{-Cl-HStb}^+)$ (**3**).



(d) FT-IR spectrum of $(\text{bta}^{2-}) \cdot 2(4\text{-OH-HStb}^+)$ (**4**).

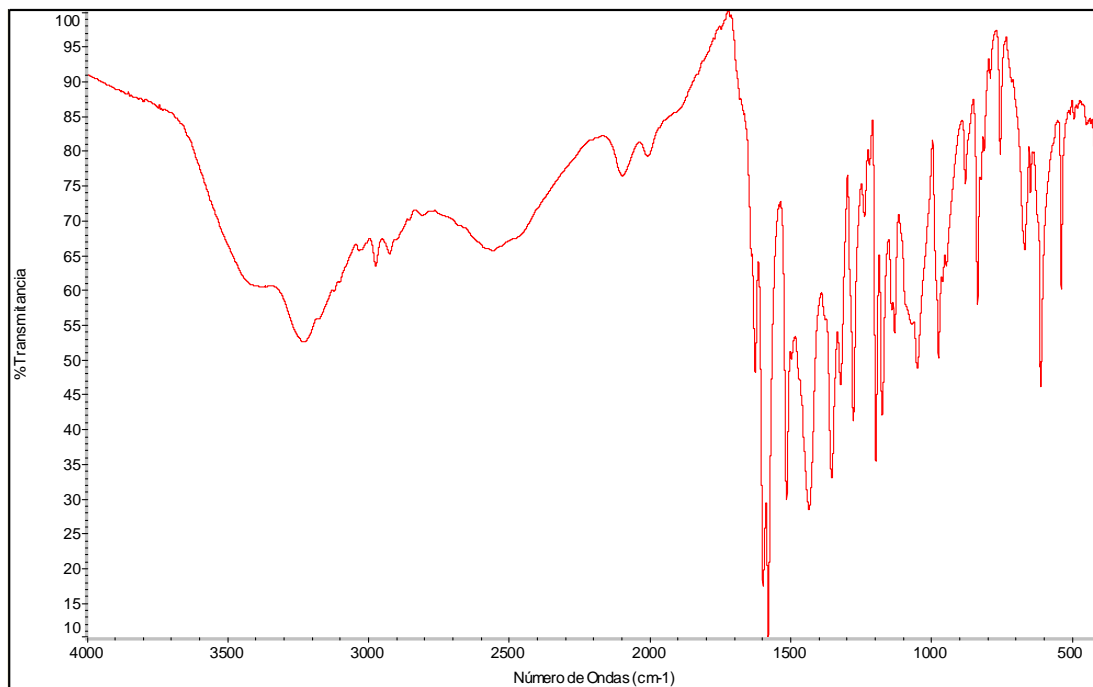


Figure S2. ^1H NMR spectrum of the mixture of products (hh and ht-isomers) obtained from the photoreaction of compound $(\text{bta}^{2-})\cdot 2(3,4\text{-bpe}^+)$ (**1**).

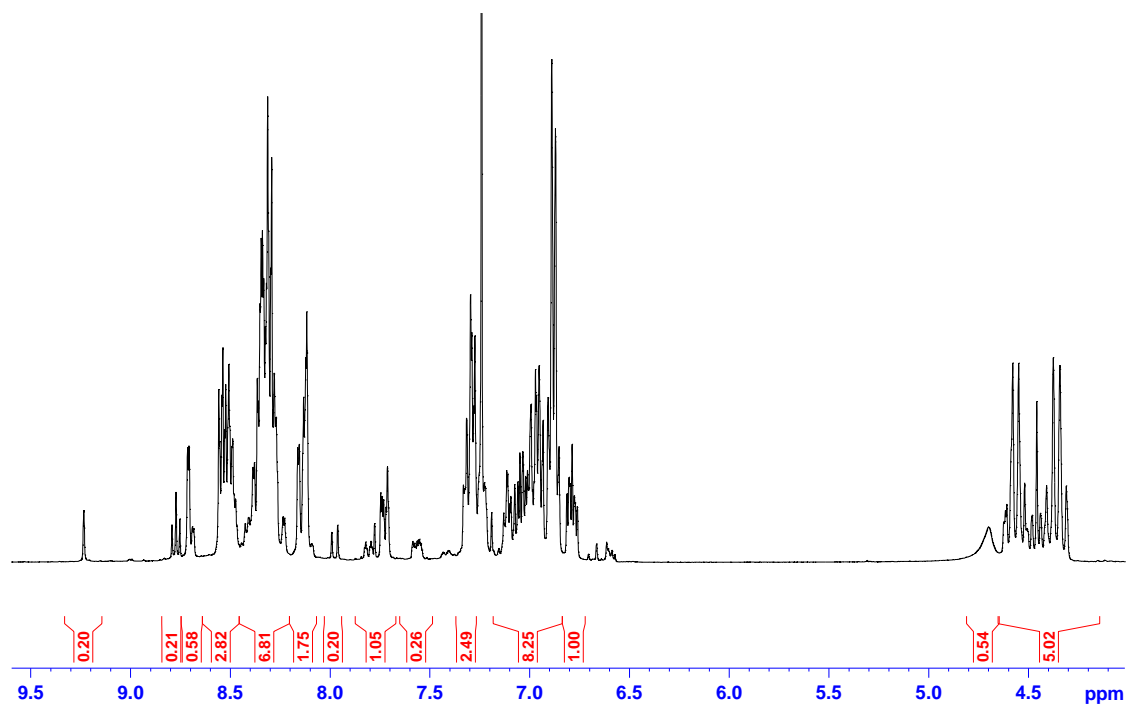


Figure S3. ^1H NMR spectrum of the ht-isomer: (*rctt*-1,3-bis(4-pyridyl)-2,4-bis(phenyl)cyclobutane) obtained from the photoreaction of compound $(\text{bta}^{2-})\cdot 2(4\text{-HStb}^+)$ (**2**).

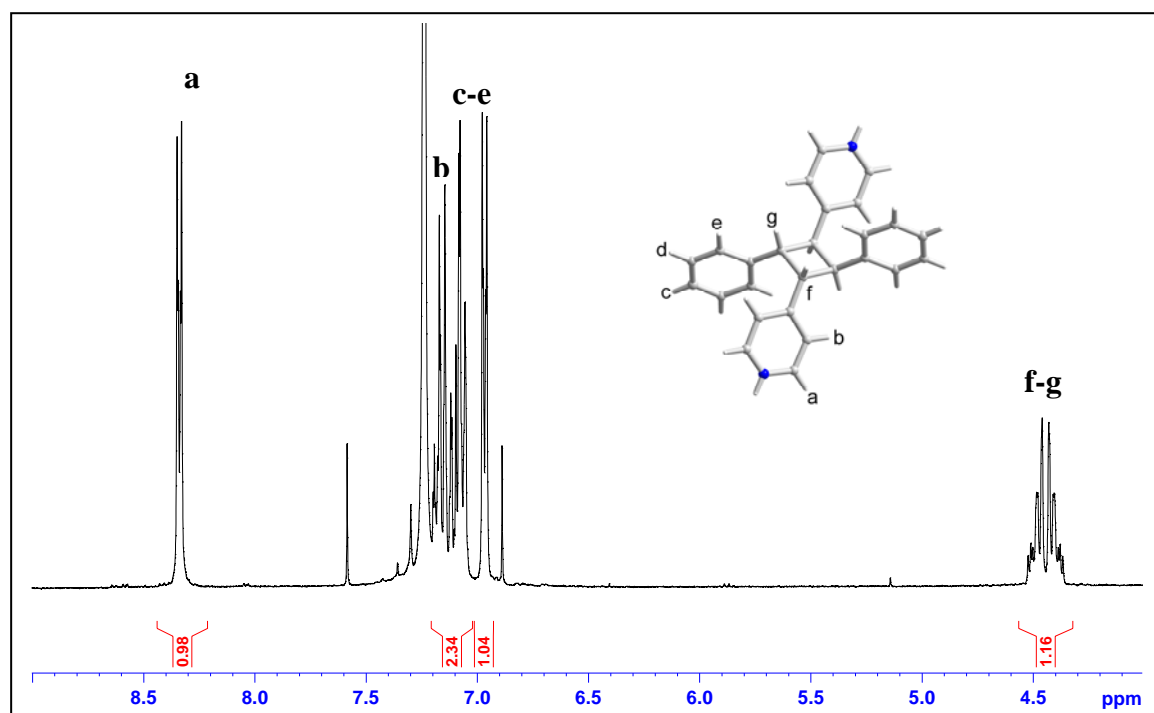


Figure S4. ^1H NMR spectrum of irradiated sample of $(\text{bta}^{2-})\cdot 2(4\text{-Cl-HStb}^+)$ (**3**), containing the ht-dimer: *rc*tt-1,3-bis(4-pyridyl)-2,4-bis(4-chlorophenyl)cyclobutane.

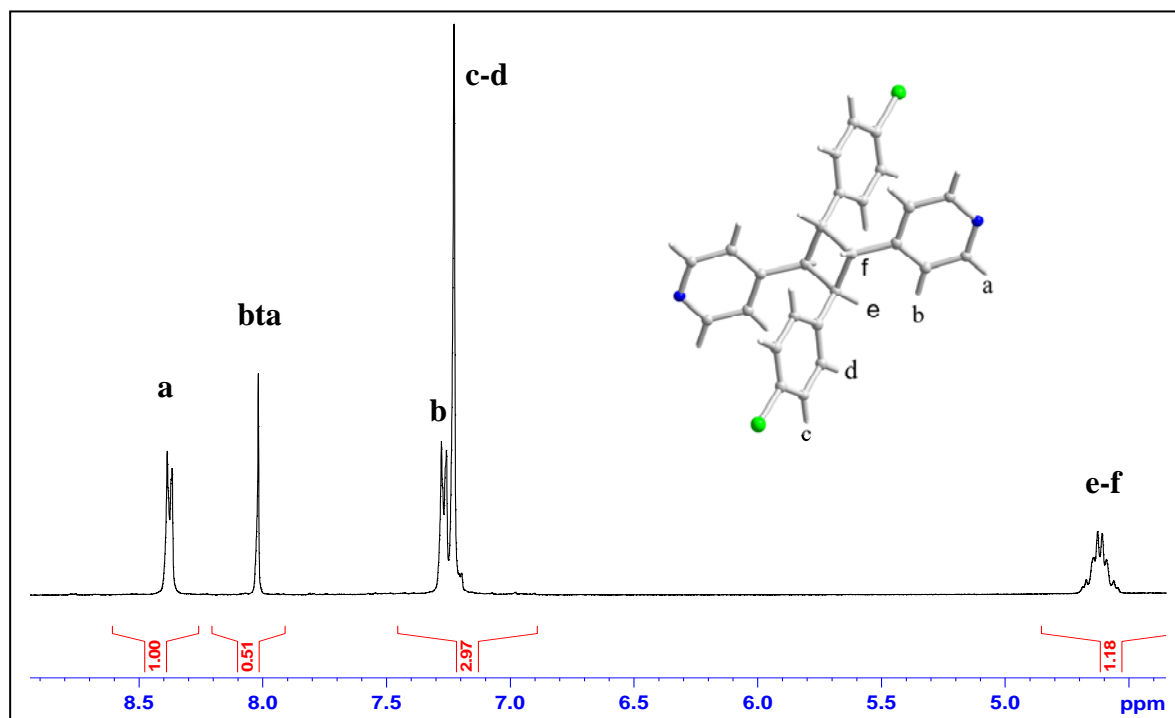


Figure S5. ^1H NMR spectrum of irradiated sample of $(\text{bta}^{2-})\cdot 2(4\text{-OH-HStb}^+)$ (**4**)

