Electronic Supplementary Information (ESI)

Observance of a large conformational change associated with the rotation of the naphthyl groups during the photodimerization of criss-cross aligned C=C bonds within a 2D coordination polymer

Fei-Long Hu,[a,b] Shu-Long Wang,[a] Brendan F. Abrahams[c] and Jian-Ping Lang*[a]

[a] *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China*

[b] *College of Chemistry and Material, Yulin Normal University, Yulin 537000, P. R. China*

[c] *School of Chemistry, University of Melbourne, Victoria 3010, Australia.*

Correspondence and requests for materials should be addressed to J.P.L. (email: jplang@suda.edu.cn)

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Experimental

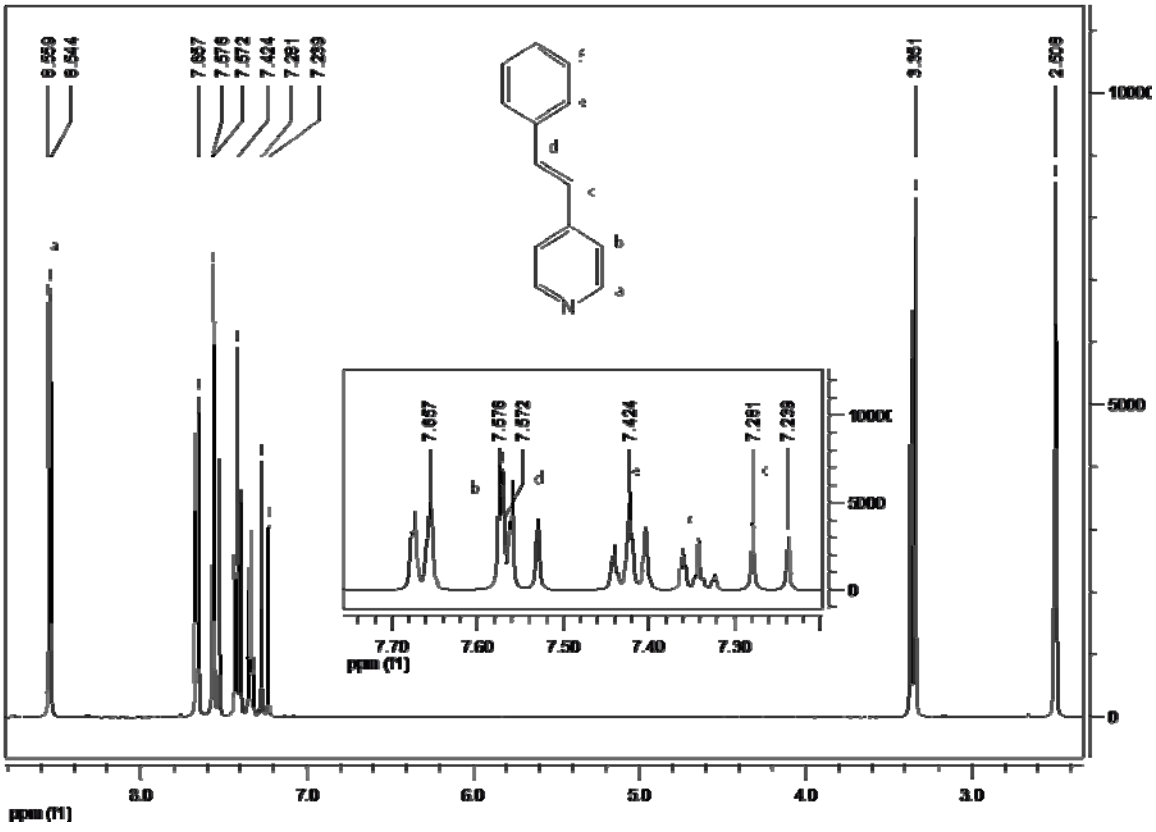
1. Preparation of 4-spy, (E)-4-(2-(naphthalen-2-yl)vinyl)pyridine 4-(2-npy) and (E)-4-(2-(naphthalen-1-yl)vinyl)pyridine (4-npy). Corresponding bromomethyl derivatives were treated with triphenylphosphine in toluene. The resulting product mixed with pyridylaldehyde in sodium hydrate solution and stirred for 20h. The crude product was obtained by evaporation of the solvents in vacuo. The mixture was loaded on a column filled with silica gel and eluted with ethyl acetate/ mineral ether (2:1). ^{1}H NMR (400MHz, DMSO, TMS): **4-spy**, δ 8.56 (d, 2H, py-H), 7.6 (d, 2H, py-H), 8.57 (d, 2H, Ph-H) 7.56 (d, 1H, C=C), 7.3-7.4 (m, 5h, Ph-H), 7.28 (d, 1H, C=C). **4-(2-npy)**, δ 8.6 (d, 2H, py-H), 8.1 (s, 1H, naphthalene-H), 7.9 (m, 4H, naphthalene-H), 7.7(1H, C=C), 7.6(2H, py-H), 7.5(2H, naphthalene-H), 7.4(1H, C=C). **4-npy**, δ 8.6 (d, 2H, py-H), 8.46 (d, 1H, naphthalene-H), 8.39 (d, 1H, C=C), 7.94 (m, 5h, naphthalene-H), 7.75 (dd, 2H, py-H), 7.59 (m, 5h, naphthalene-H), 7.32 (d, 1H, C=C) (Figures S1).

2. Computational method

Gas phase structure optimizations were carried out using DFT as implemented in the Gaussian 09 package with the B3LYP functional using 6-31G* basis sets.[1]

References

1. M. J. Frisch, et al. Gaussian 09, Revision A.02; Gaussian, Inc.: Wallingford, CT, **2009**



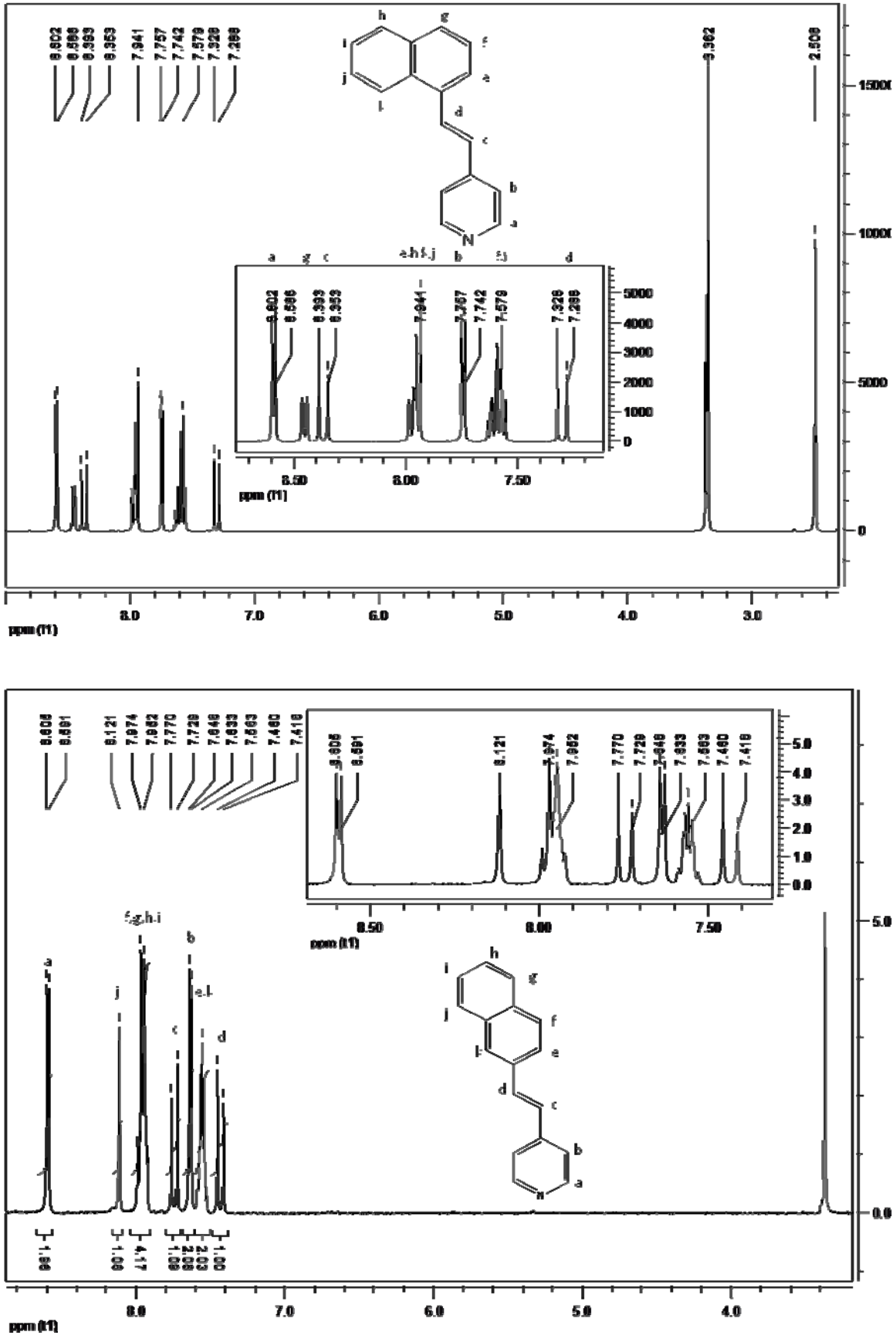


Figure S1. The ^{1}H NMR spectrum of 4-spy, 4-npy and 4-(2-npy).

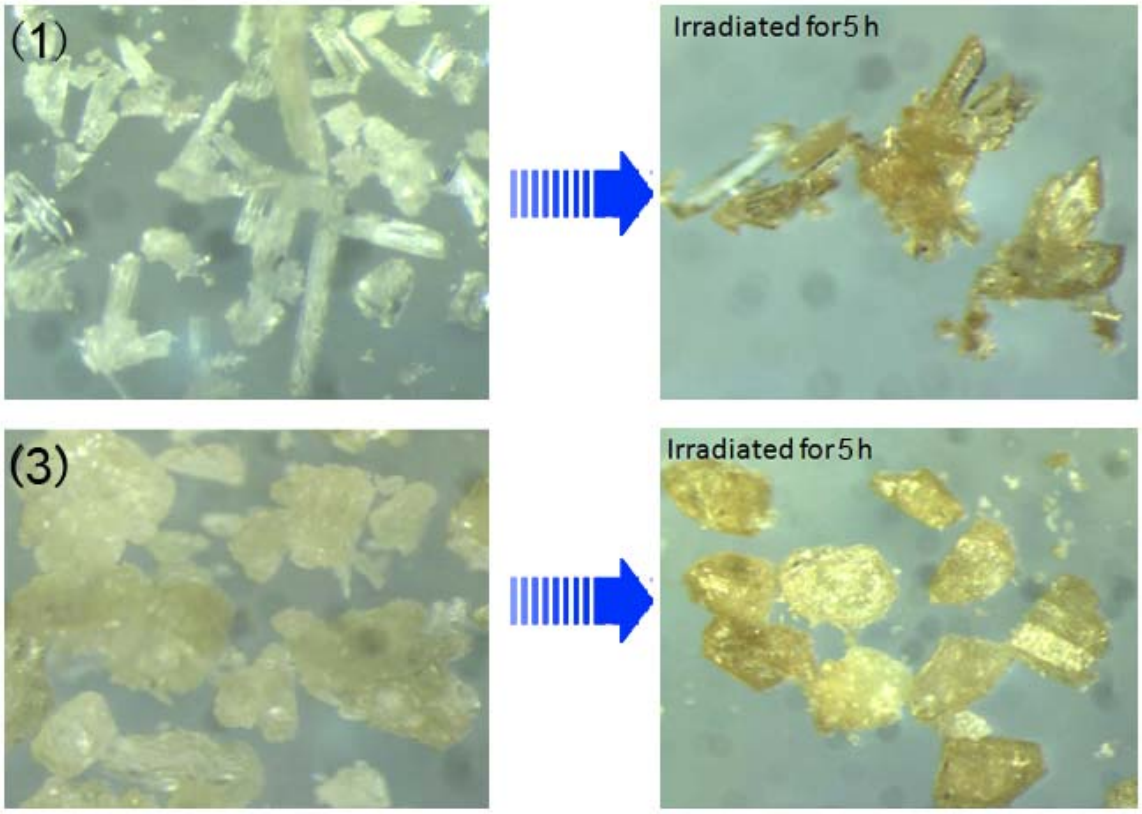


Figure S2. The photos of **1**, **1a** (**1** irradiated for 5h), **3** and **3a** (**3** irradiated for 5h).

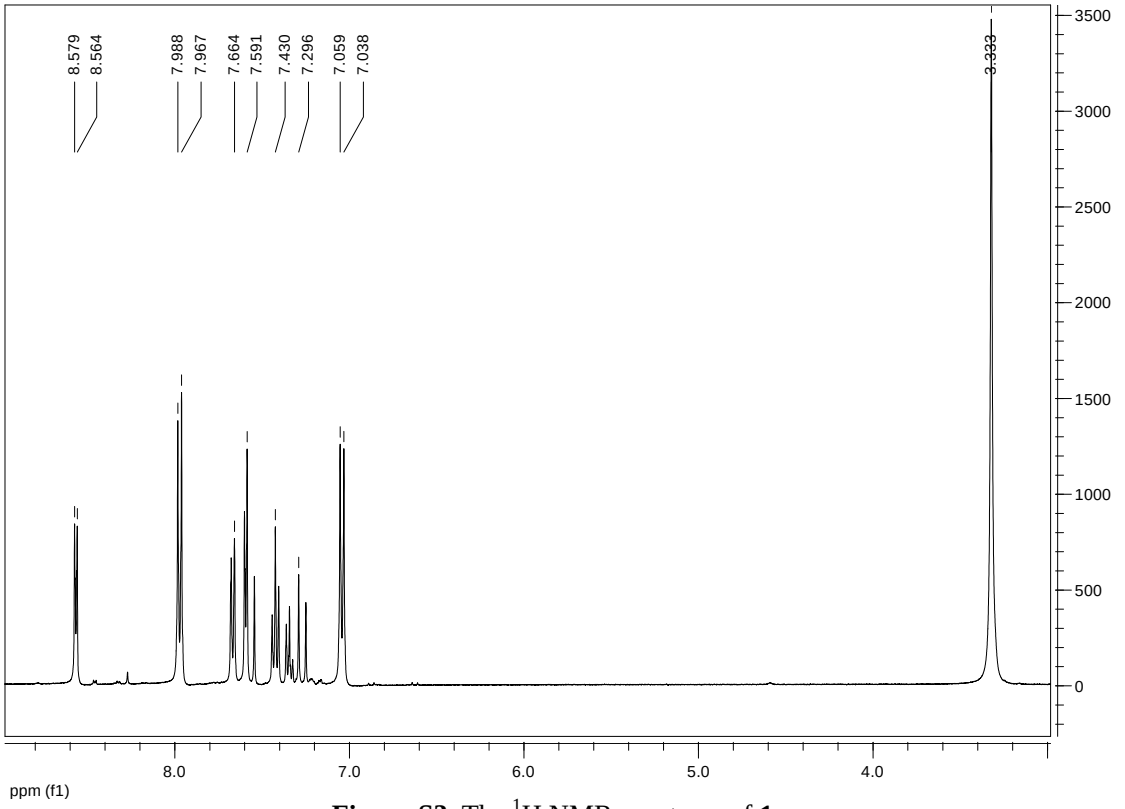


Figure S3. The ^{1}H NMR spectrum of **1**.

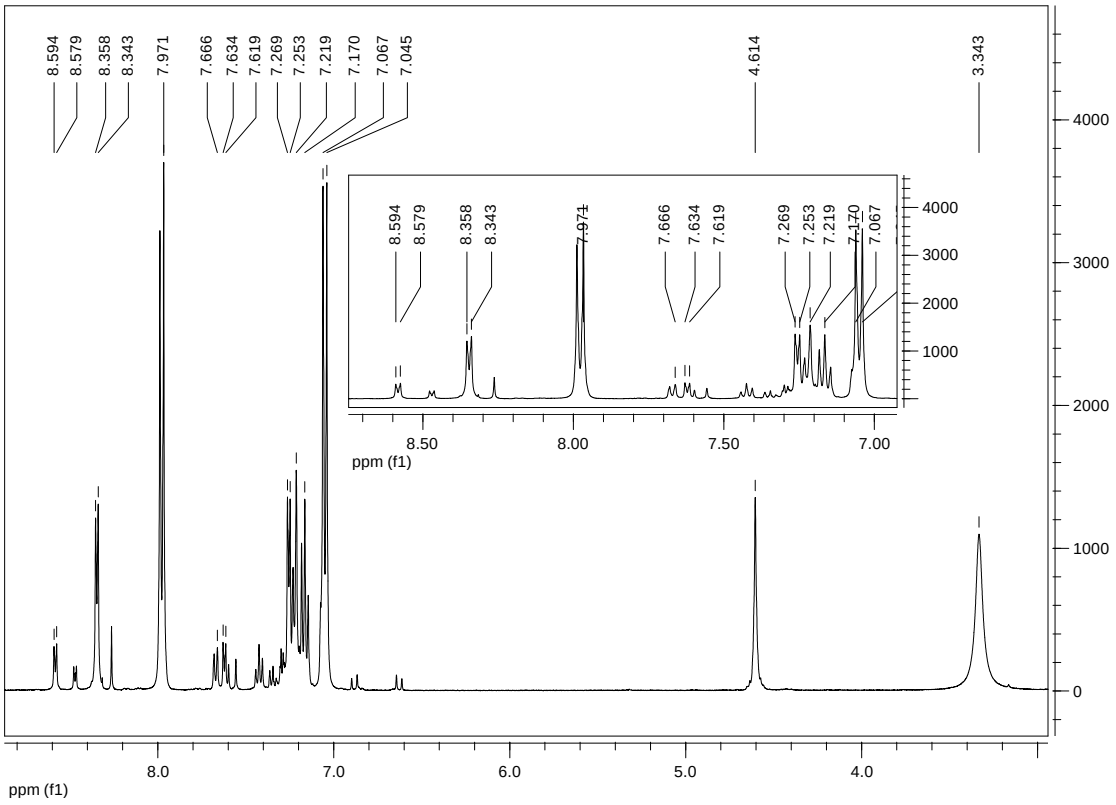


Figure S4. The ^{1}H NMR spectrum of **1a**.

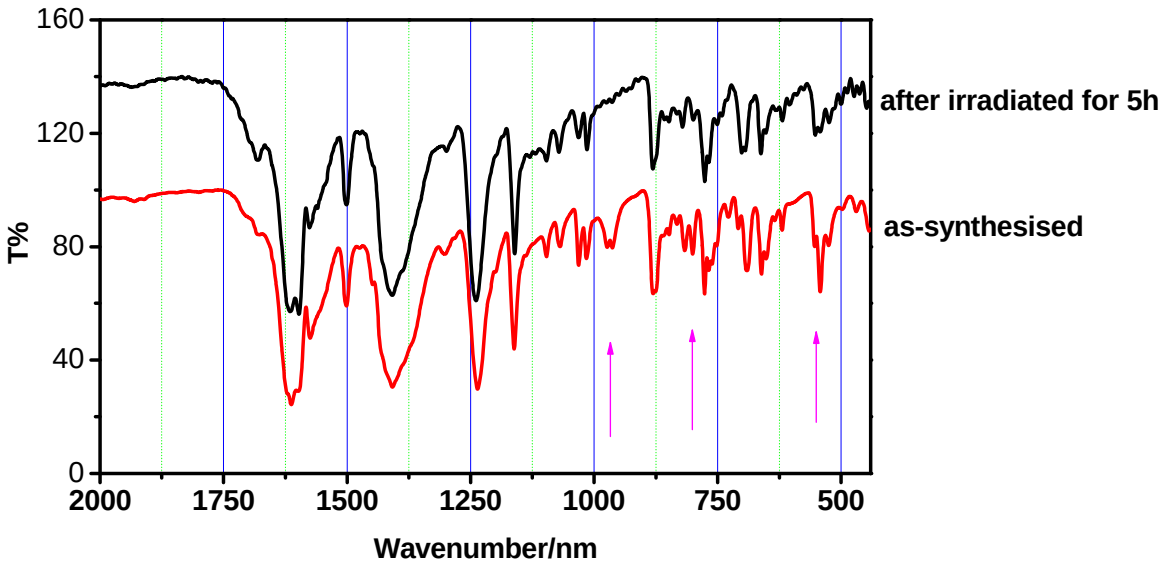


Figure S5. IR spectra of crystal samples of **1** and **1a** (irradiated by UV light for 5h).

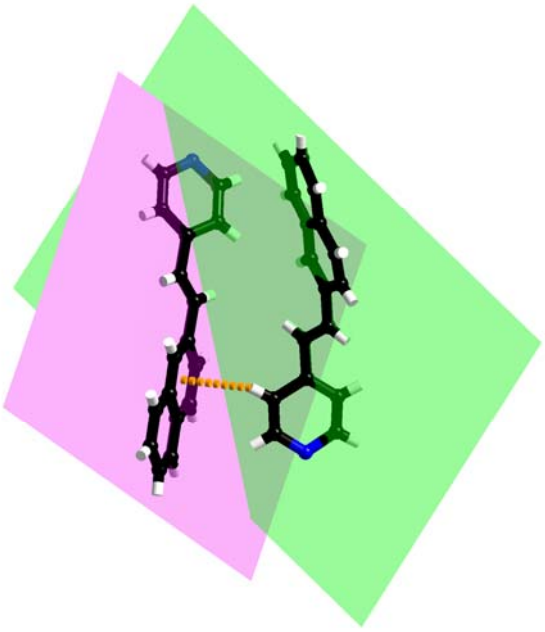


Figure S6. Pespective view showing the angle of 4-(2-npy) is 85.44° and the edge-to-face interaction.

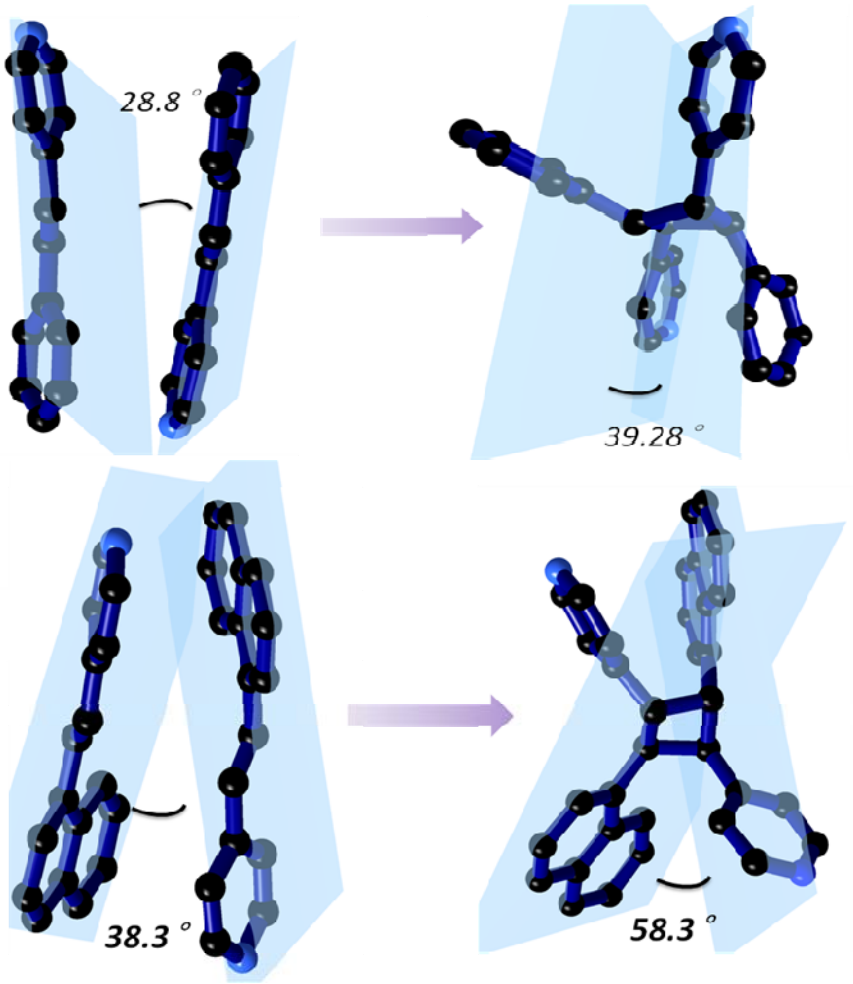


Figure S7. (top) The dihedral angle between the Py rings in **1** and **1a**. (bottom) The dihedral angle between the naphthalene molecules in **3** and **3a**.

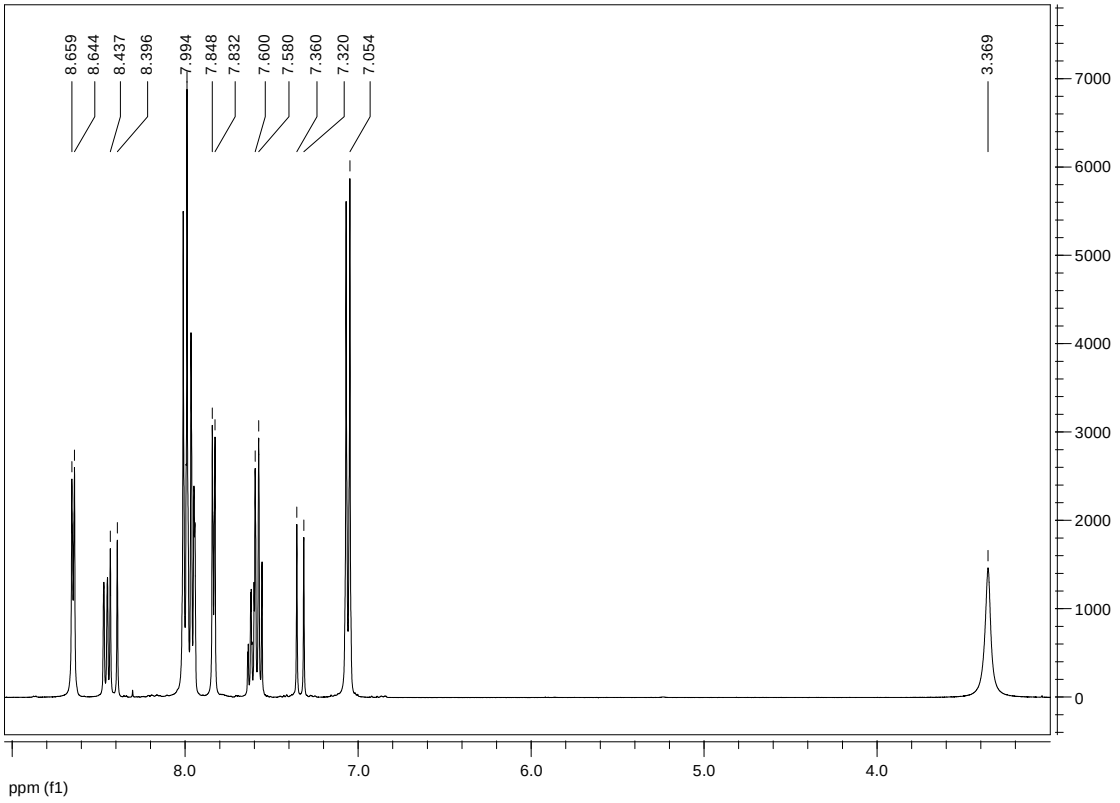


Figure S8. The ^{1}H NMR spectrum of **3**.

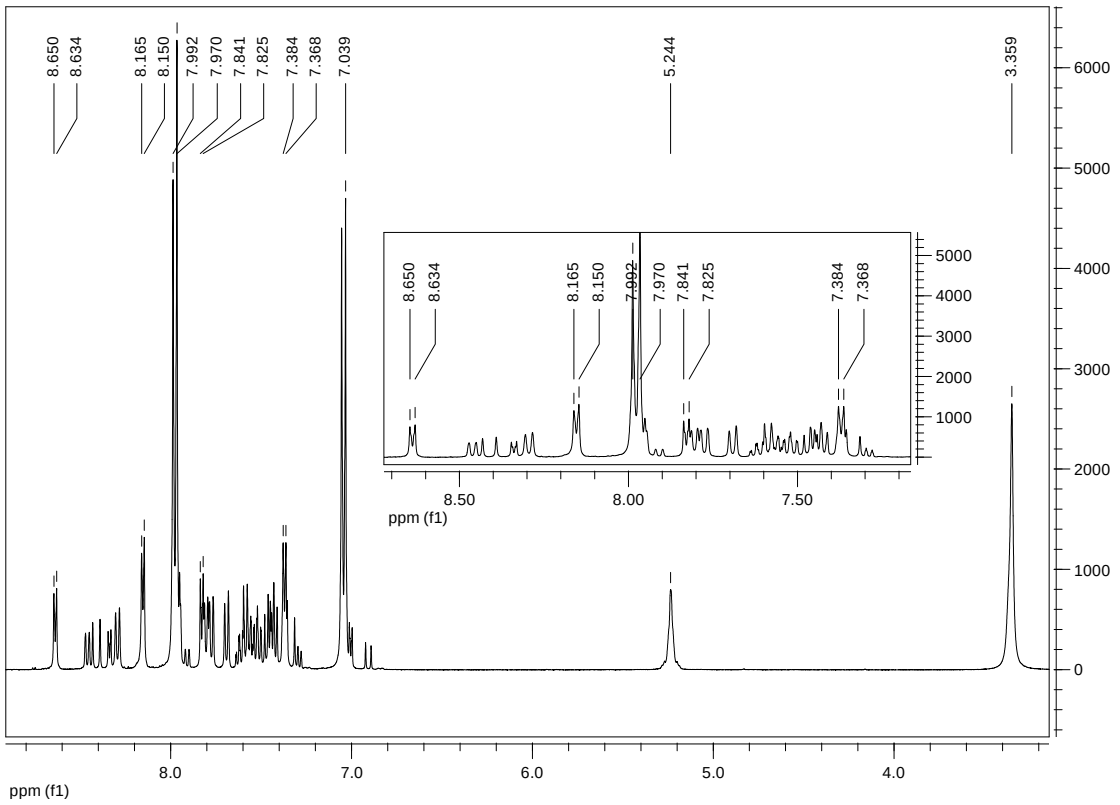


Figure S9. The ^{1}H NMR spectrum of **3a.**

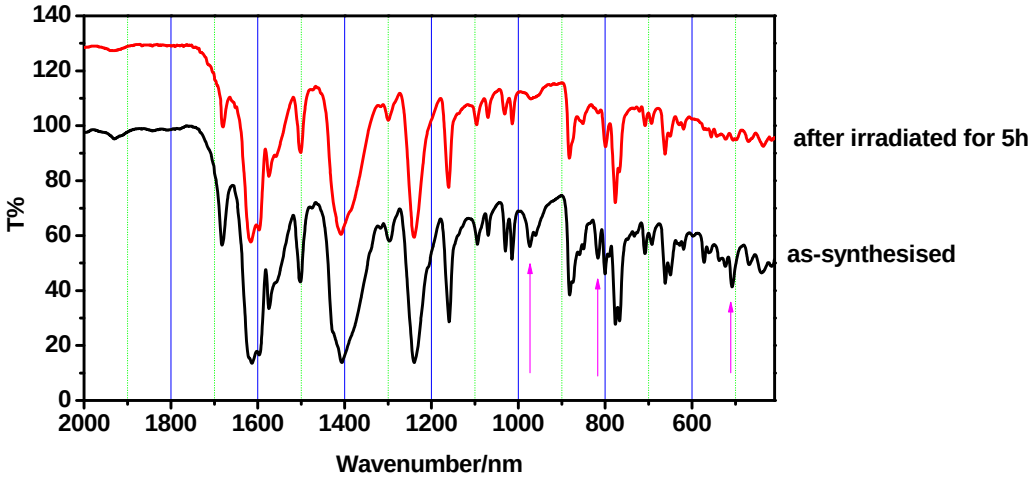


Figure S10. IR spectra of crystal samples of **3** and **3a** (irradiated by UV light for 5h).

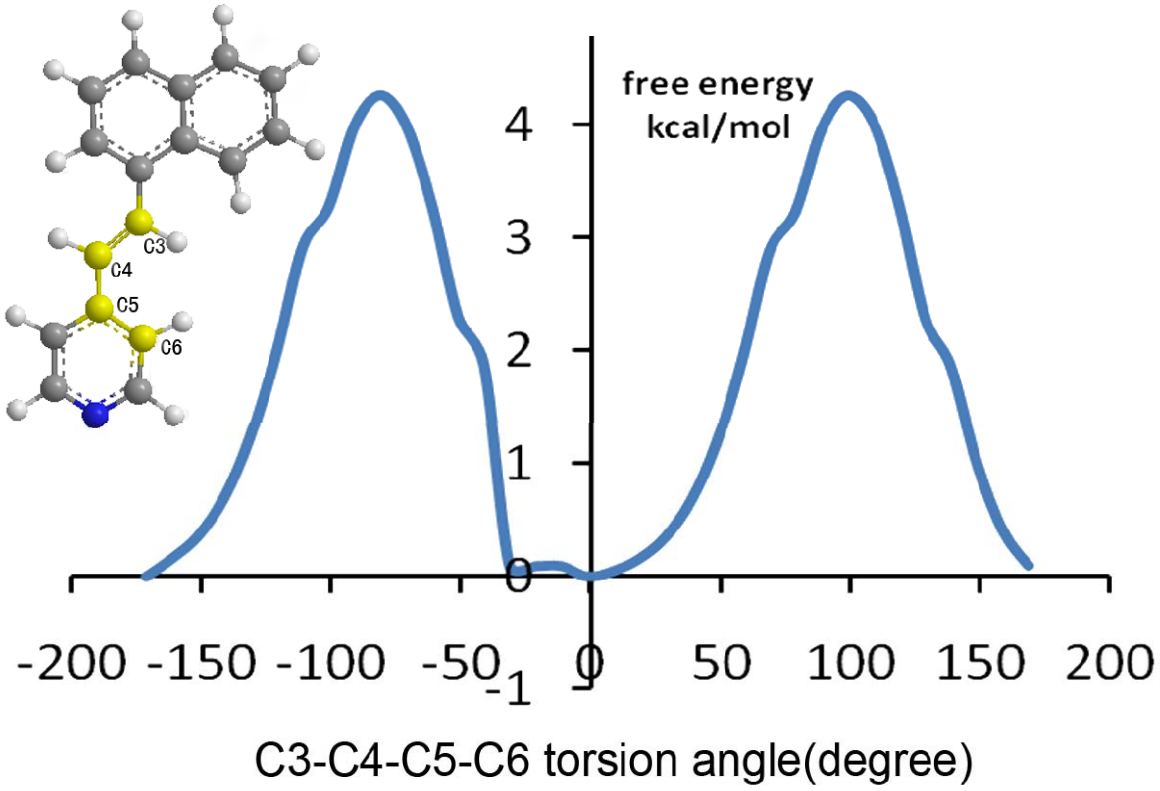


Figure S11. Potential energy profile for the C3-C4-C5-C6 bond of npy calculated at the B3LYP/6-31G(d) level.

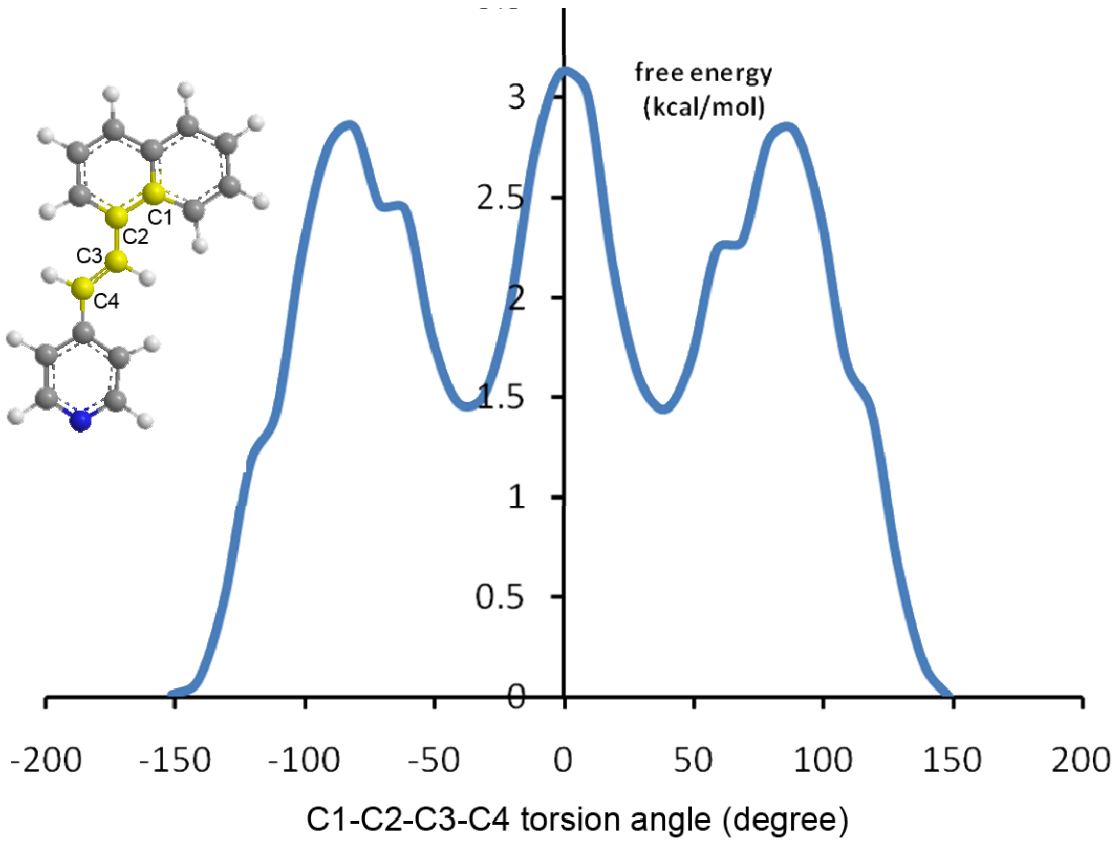


Figure S12. Potential energy profile for the C1-C2-C3-C4 bond of npy calculated at the B3LYP/6-31G(d) level.

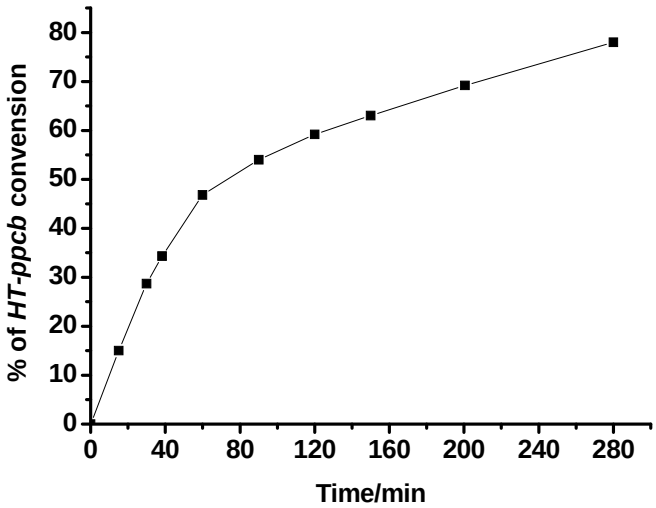


Figure S13. Ratio of the irradiated products in **1**.

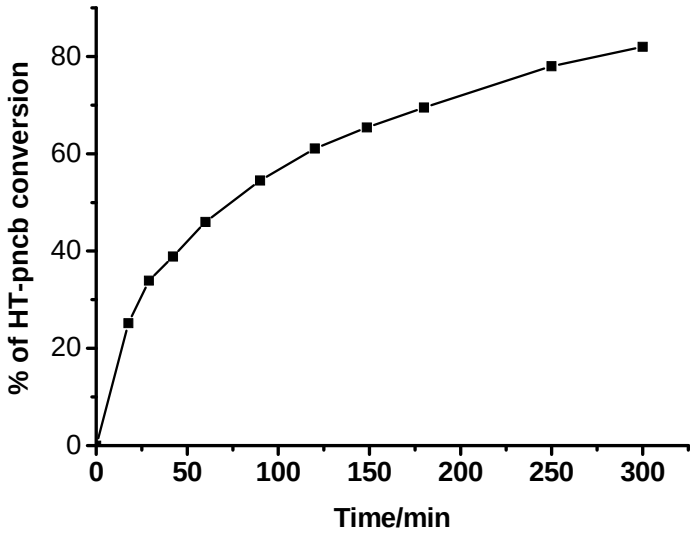


Figure S14. Ratio of the irradiated products in **3**.

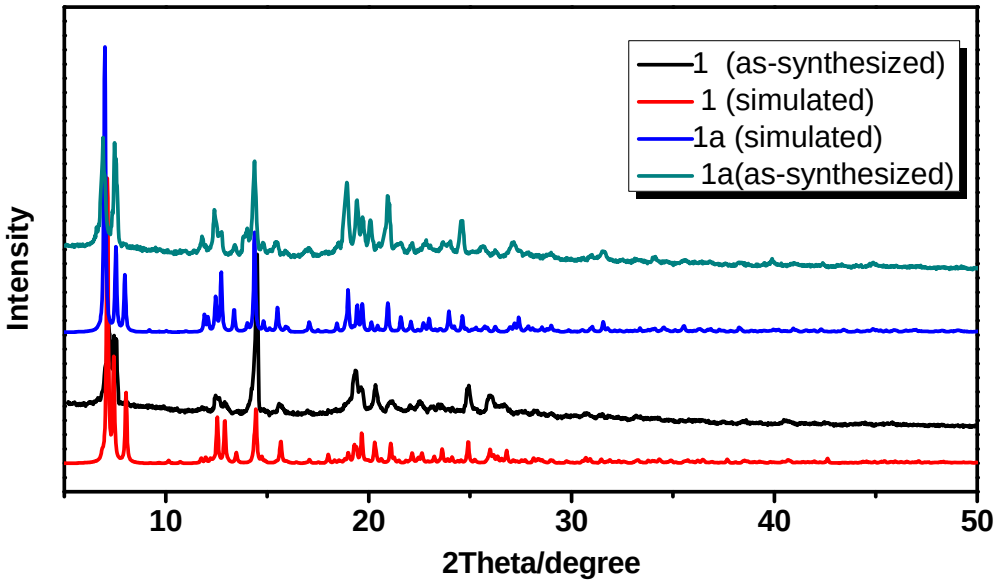


Figure S15. Experimental (cyan (**1**) and black (one sample irradiated for 5h)) and simulated (red (**1**) and blue (**1a**)) PXRD patterns.

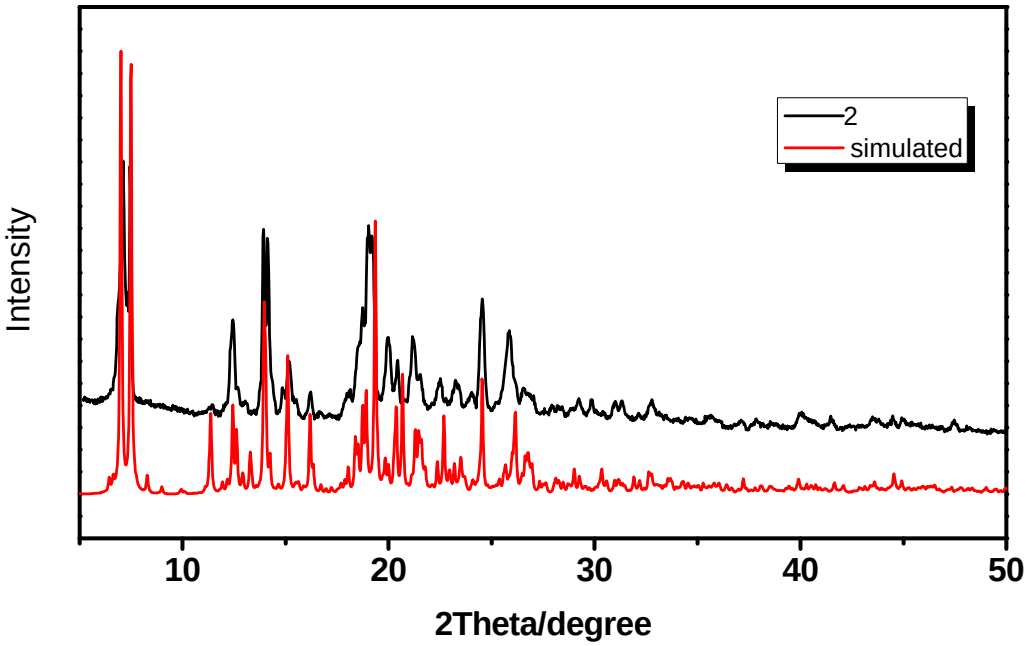


Figure S16. Experimental (black (**2**)) and simulated (red (**2**)) PXRD patterns.

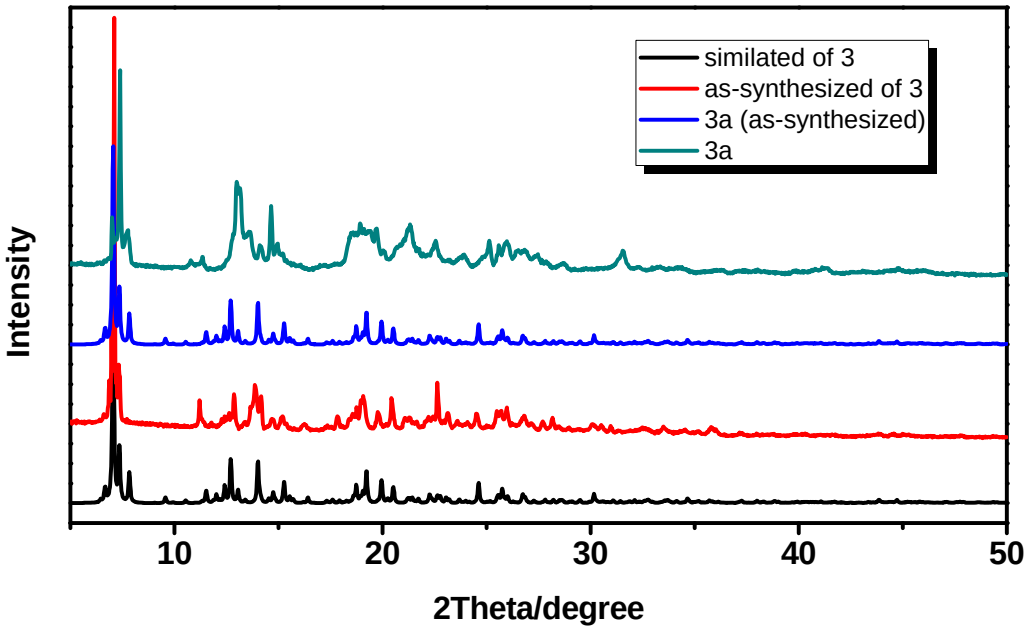


Figure S17. Experimental (red (**3**) and cyan (one sample irradiated for 5h)) and simulated (black (**3**) and blue (**3a**)) PXRD patterns.

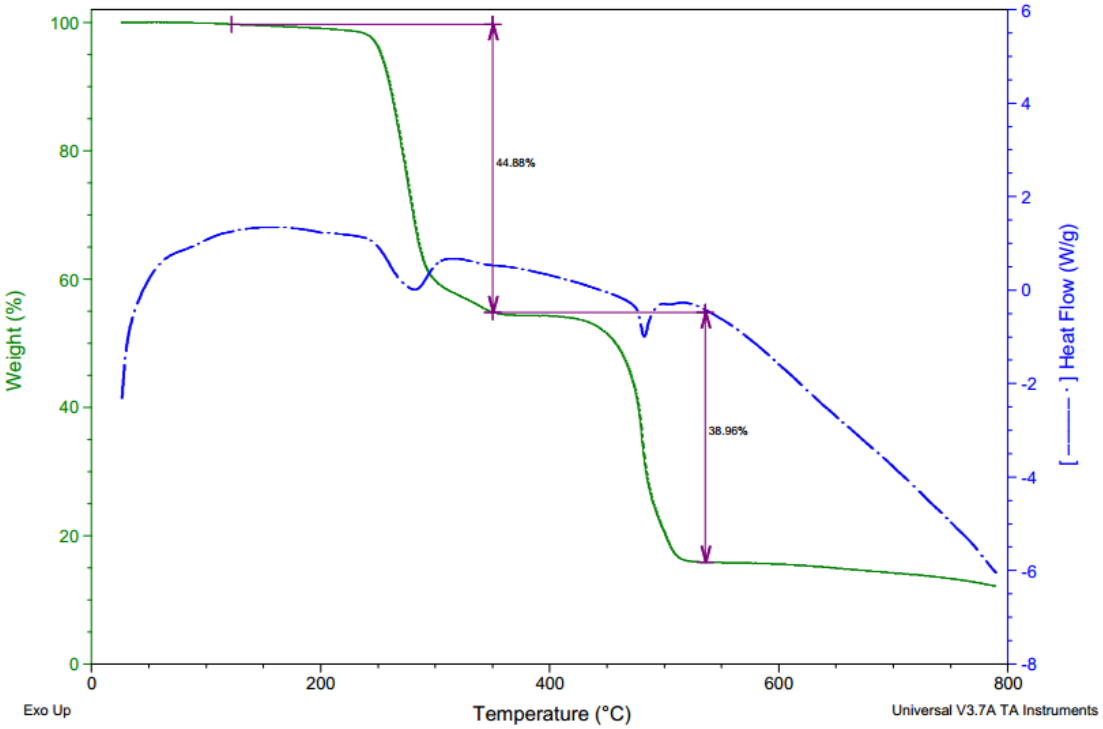


Figure S18. TG (green) and DSC (blue) curves of **1**.

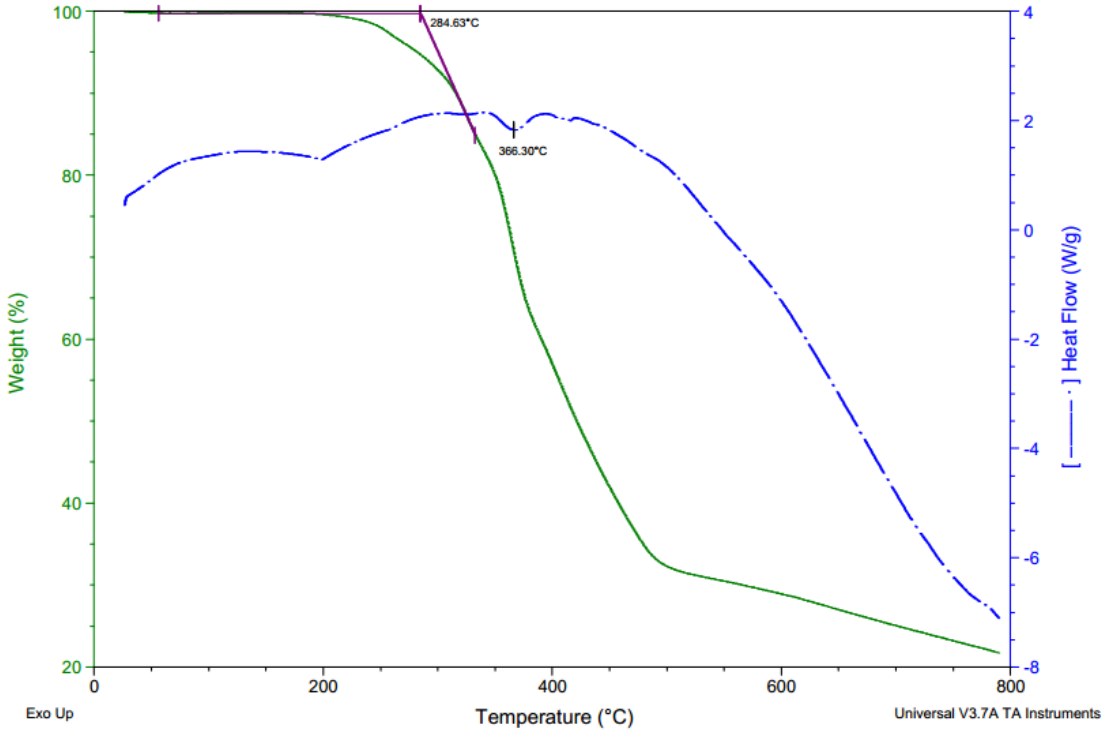


Figure S19. TG (green) and DSC (blue) curves of **1a**.

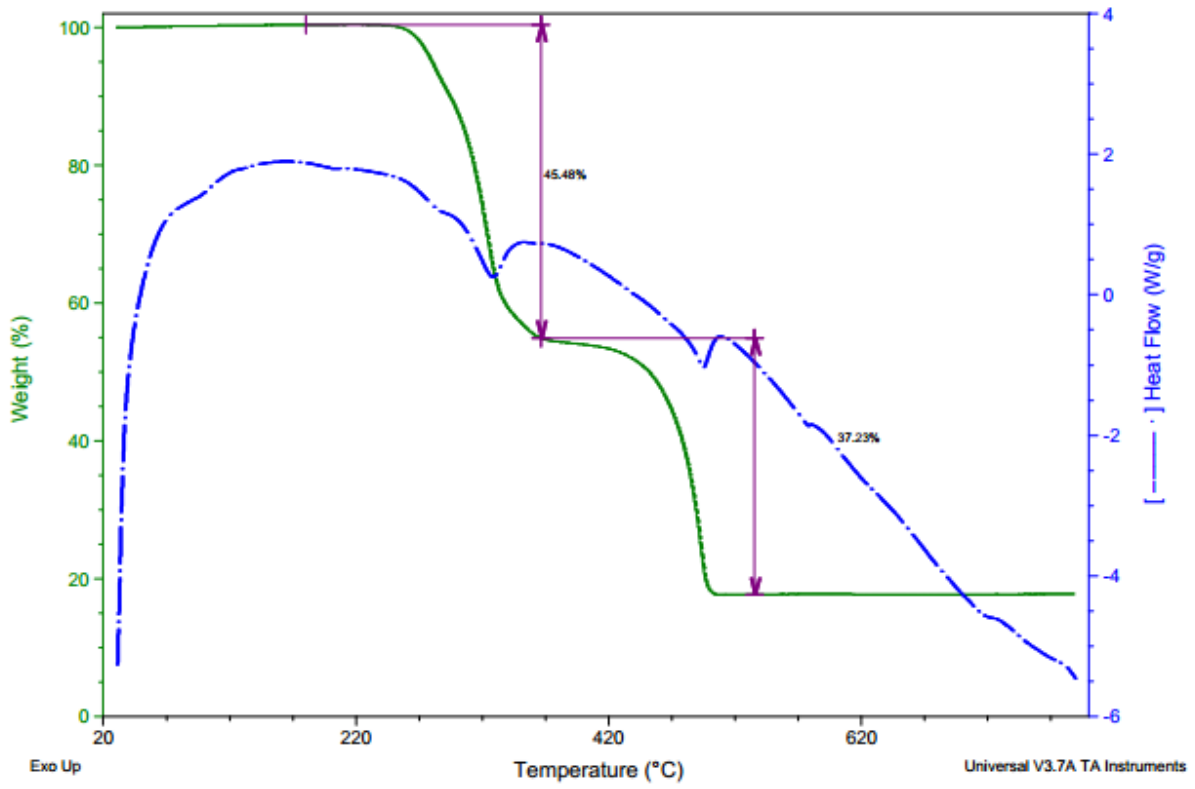


Figure S20. TG (green) and DSC (blue) curves of **2**.

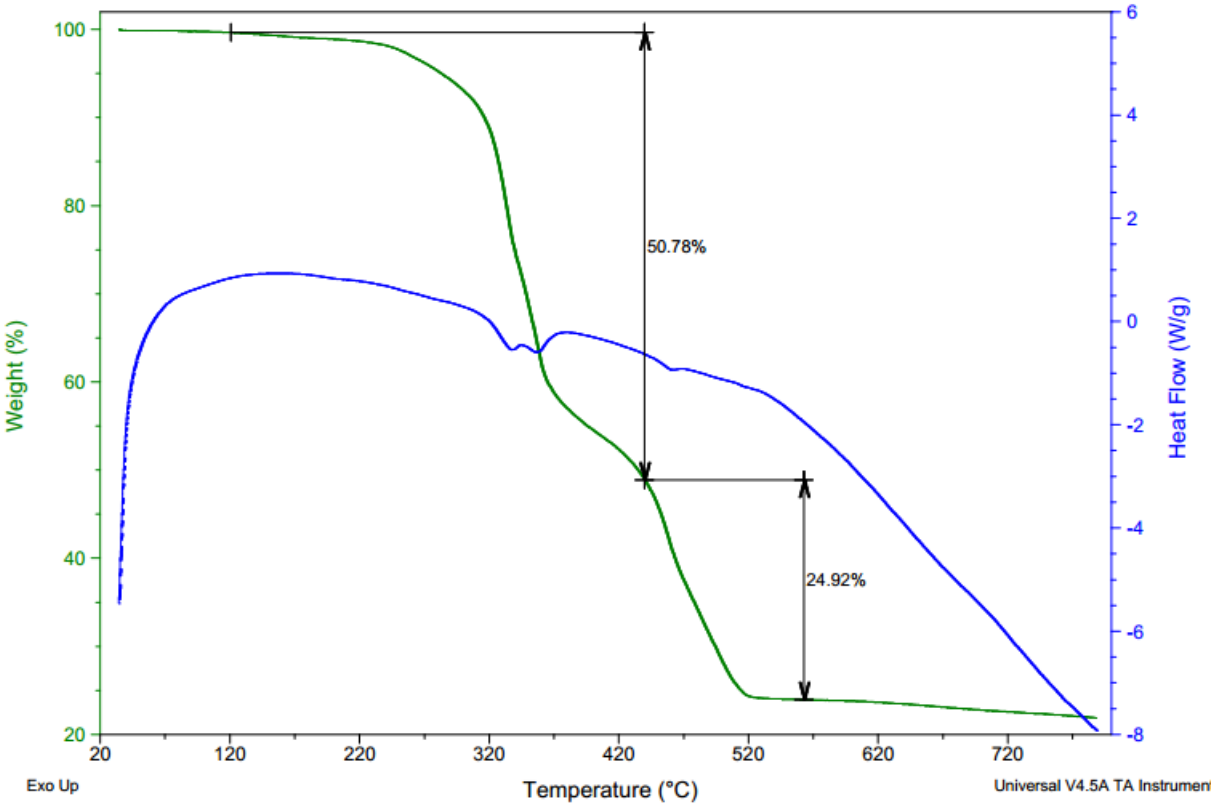


Figure S21. TG (green) and DSC (blue) curves of **3**.

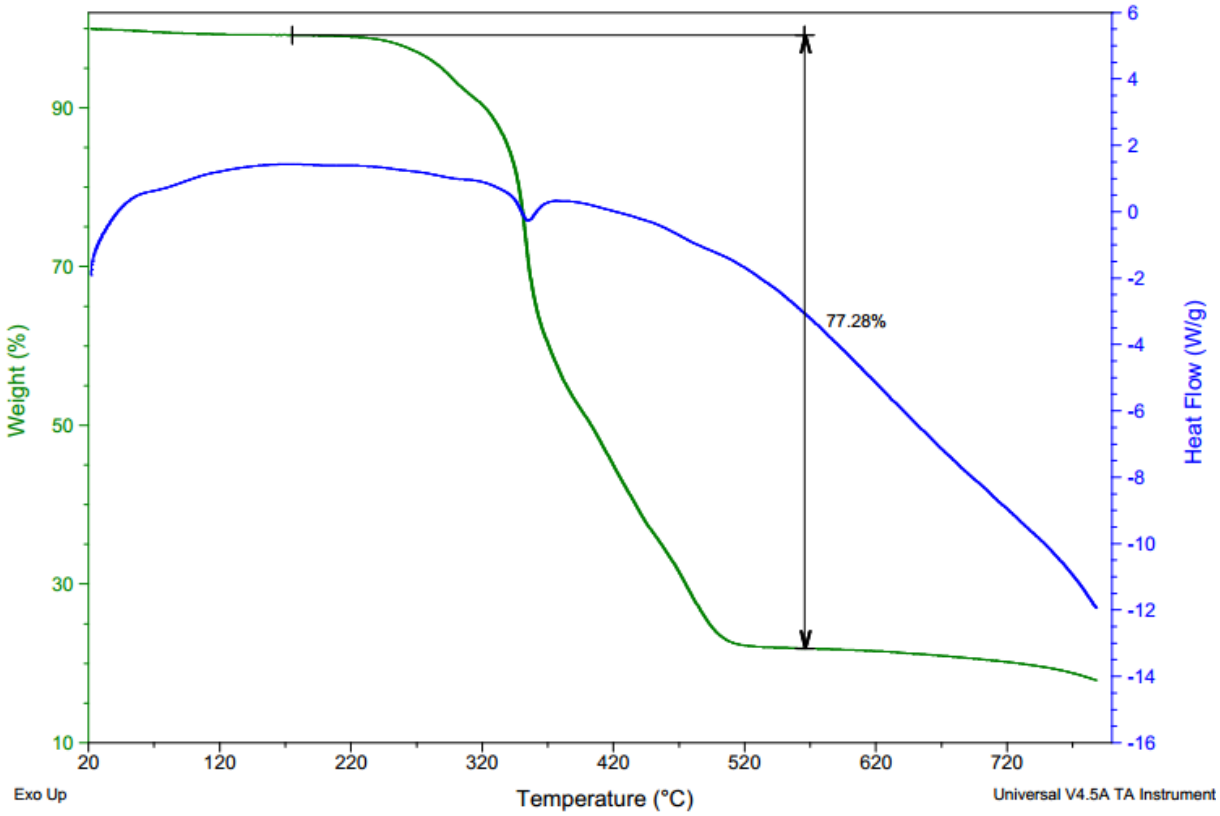


Figure S22. TG (green) and DSC (blue) curves of **3a**.

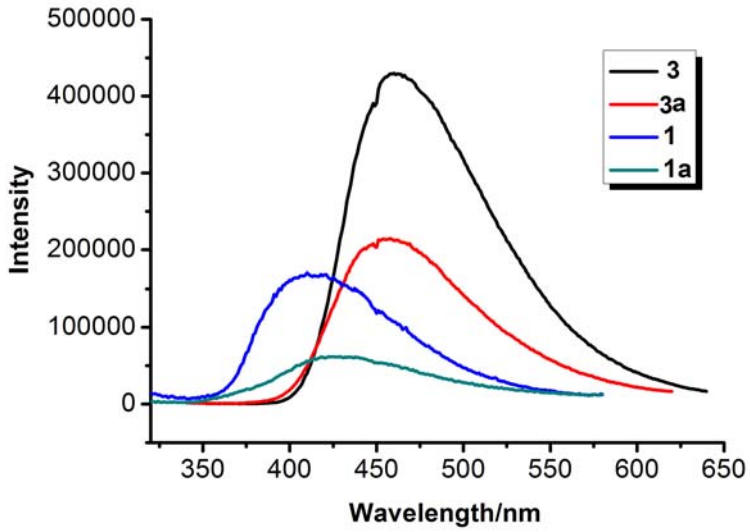


Figure S23. Solid state emission spectra of complexes **1, 1a, 3** and **3a**.