Supporting Information:

Squaraine Derived Rotaxanes: Sterically Protected Fluorescent Near-IR Dyes

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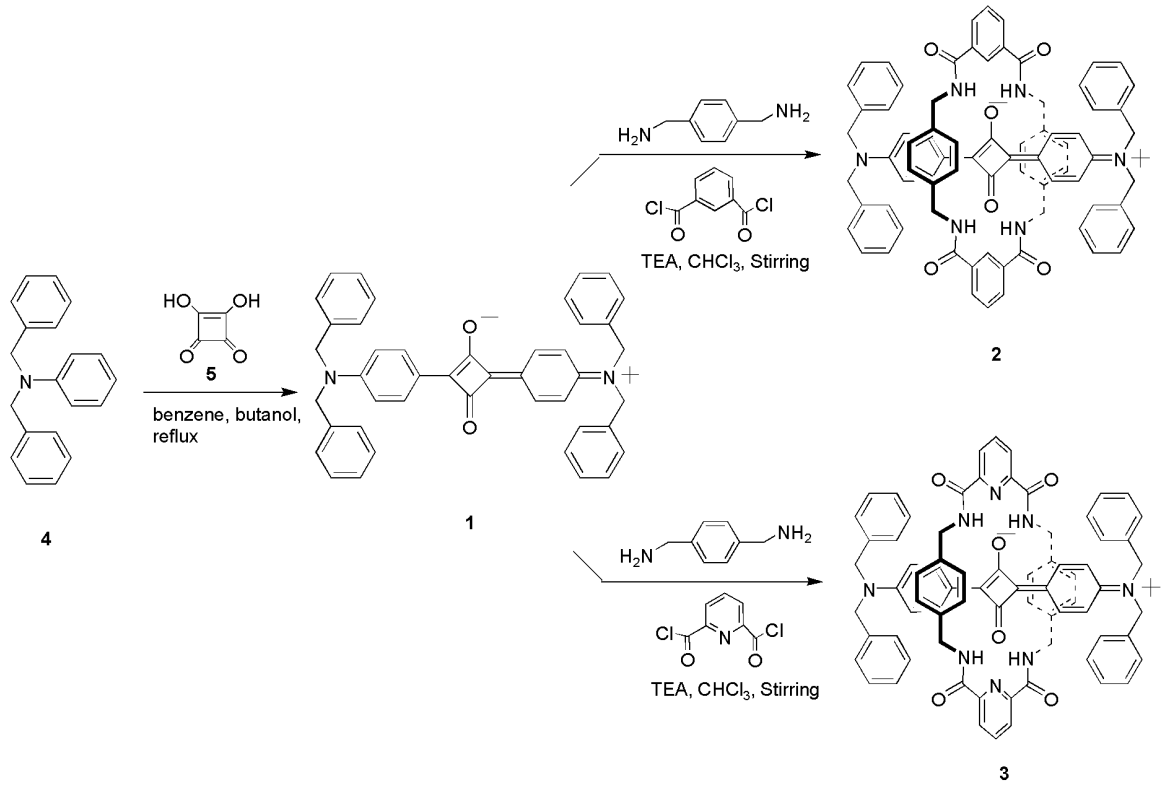
A. Synthesis



***Scheme S1*:** Synthesis of squaraine **1** and rotaxanes **2** and **3**

Procedure to synthesize squaraine dye 1

Dibenzylaniline **4** (500 mg, 1.83 mmol) was added to a solution of squaric acid **5** (104 mg, 0.92 mmol) in a mixture of *n*-butanol (15 mL) and benzene (30 mL) in a 100 mL round bottom flask equipped with a Dean Stark apparatus. The reaction mixture was refluxed, while the water formed in the reaction mixture was trapped in the Dean Stark apparatus. After 12 h the deep green colored reaction mixture was concentrated to remove the solvent and the crude product was precipitated by adding 30-40 mL hexane. After filtering, the product was washed several times with hexane to give the dark green squaraine dye **1** as a crystalline solid. Yield: 35%. mp. 275 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): □ 4.80 (s, 8H), 6.87 (d, J = 9 Hz, 4H), 7.19-7.38 (m, 20H), 8.36 (d, J = 9 Hz, 4H); ^{13}C NMR was not acquired because of poor solubility.

General procedure to synthesize rotaxanes 2 and 3

Clear solutions of the corresponding diacid dichloride (1.28 mmol) and *p*-xylylenediamine (1.28 mmol) in 5 mL chloroform were simultaneously added dropwise using a mechanical syringe pump (kd Scientific) apparatus over five hours to a stirred solution of **1** (200 mg, 0.32 mmol) and triethylamine (3.2 mmol) in 40 mL of $CHCl_3$. After stirring overnight, the reaction mixture was filtered through a pad of celite to remove any polymeric material, and the resulting crude product chromatographed using a neutral alumina column and a mixture of methanol/chloroform (1/19) as eluent.

Rotaxane 2: Yield 28%, mp > 300 °C; TLC rf = 0.5, methanol/chloroform (1/19); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): □ 4.38 (d, *J* = 5 Hz, 8H), 4.79 (s, 8H), 6.47 (d, *J* = 9 Hz, 4H), 6.66 (s, 8H), 7.16 (d, *J* = 8 Hz, 8H), 7.37 (t, *J* = 7 Hz, 4H), 7.41 (t, *J* = 8 Hz, 8H), 7.51 (t, *J* = 8 Hz, 2H), 7.69 (d, *J* = 10 Hz, 4H), 8.06 (t, *J* = 10 Hz, 4H), 8.20 (d, *J* = 10 Hz, 4H), 9.22 (s, 2H); ^{13}C NMR (125MHz, $CDCl_3$, TMS) : □ 44.1, 54.6, 113.2, 118.7, 124.5, 126.4, 128.2, 129.1, 129.2, 129.3, 131.6, 133.1, 133.9, 135.2, 136.4, 155.3, 166.0, 183.1, 184.9.

Rotaxane 3: Yield 30%, mp > 300 °C; TLC rf = 0.5, methanol/chloroform (1/19); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): □ 4.50 (d, *J* = 6 Hz, 8H), 4.67 (s, 8H), 6.26 (d, *J* = 9 Hz, 4H), 6.66 (s, 8H), 7.11 (d, *J* = 9 Hz, 8H), 7.34-7.41 (m, 20H), 7.99 (t, *J* = 8 Hz, 4H), 8.06 (d, *J* = 9 Hz, 4H), 8.37 (d, *J* = 8 Hz, 4H), 9.86 (t, *J* = 6 Hz, 2H); ^{13}C NMR (125MHz, $CDCl_3$, TMS) : □ 43.4, 54.5, 112.7, 120, 125.3, 126.6, 128.2, 129, 129.4, 133.8, 135.7, 136.9, 138.7, 149.4, 155.1, 163.6, 185, 186.3.

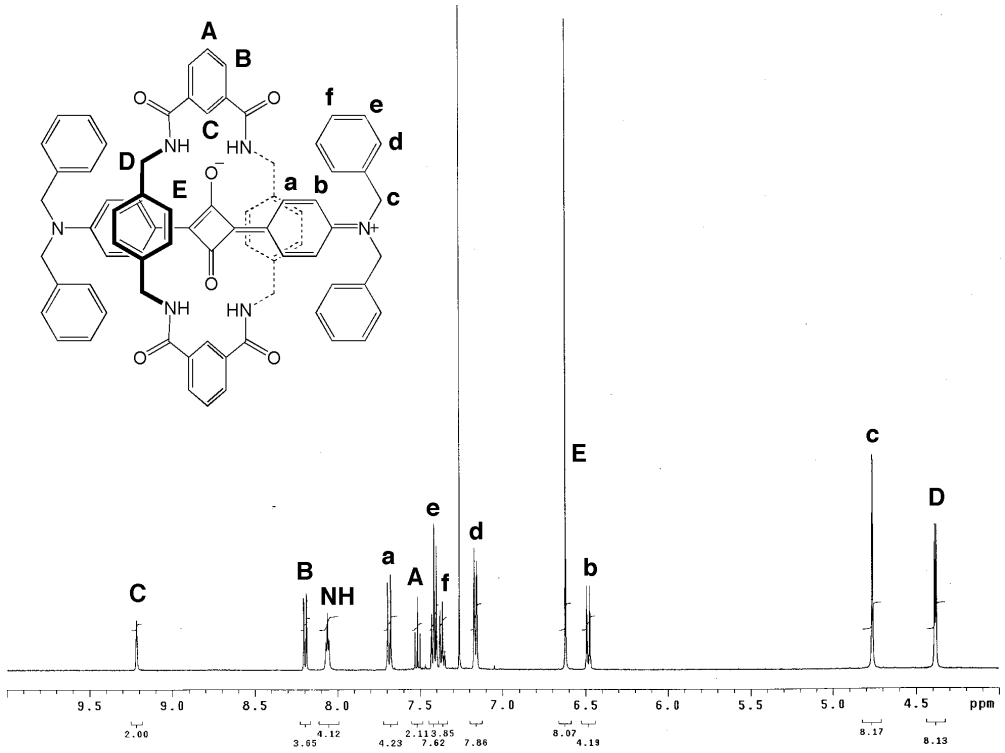


Figure S1:[1]H NMR spectrum of **2** in $CDCl_3$ (500 MHz).

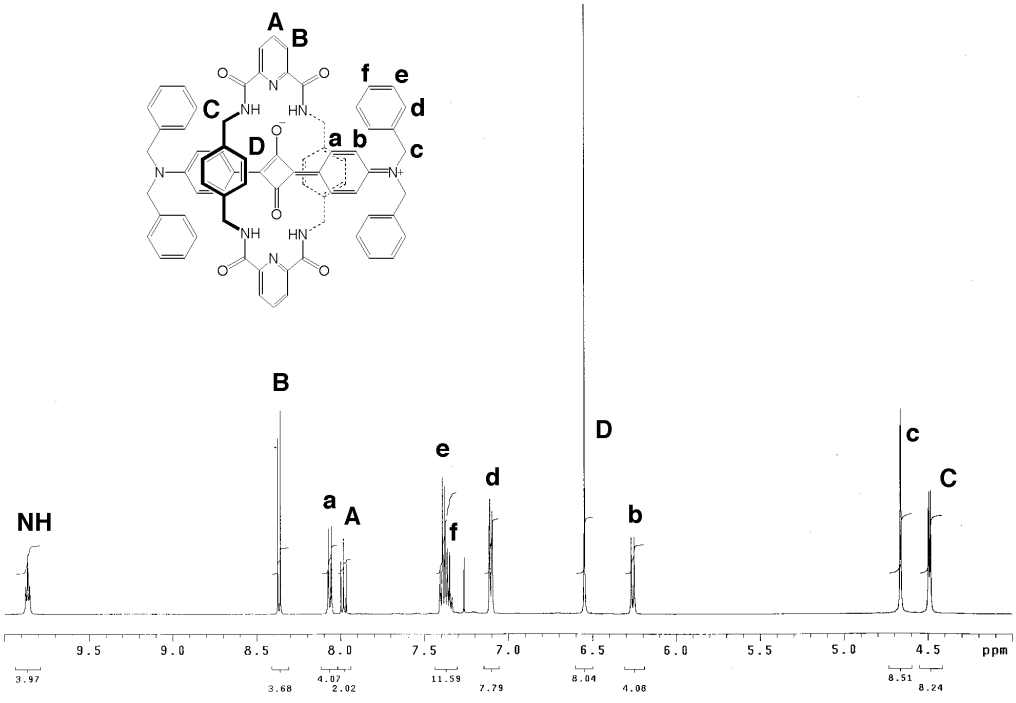


Figure S2:[1]H NMR spectrum of **3** in $CDCl_3$ (500 MHz).

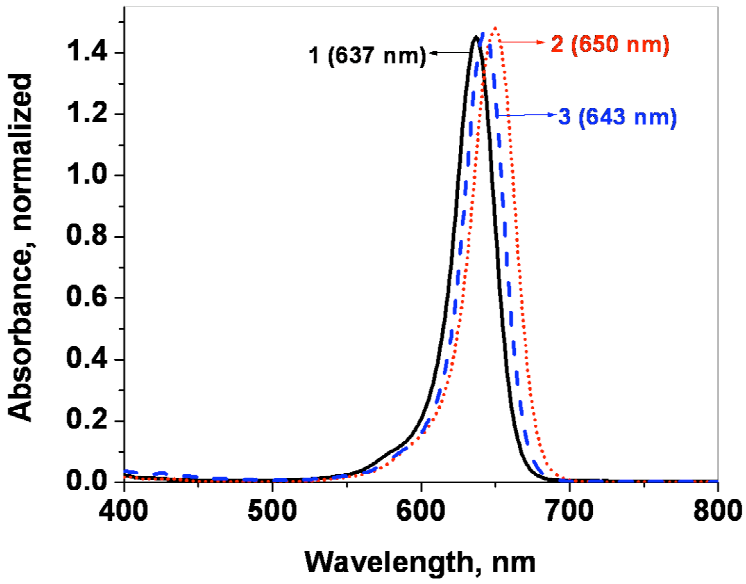


Figure S3: Absorption spectra of **1**, **2** and **3** in THF:Water (4:1) mixture.

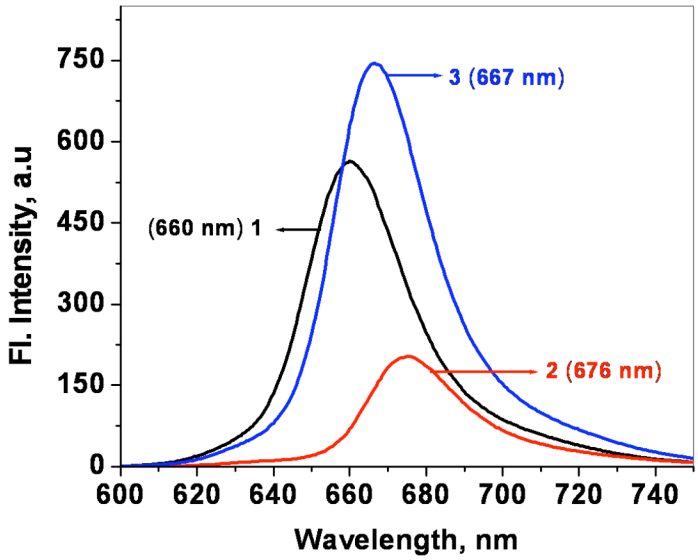


Figure S4: Fluorescence emission spectra of **1**, **2** and **3** in THF:Water (4:1) mixture, ex: 580 nm.

B. X-ray Structures

Isophthalamide-containing rotaxane 2

Single crystal was obtained from the slow diffusion of cyclohexane into a solution of **2** in chloroform. Crystallographic summary: monoclinic, $C_{80}H_{68}Cl_{12}N_6O_6$, M_r = 1634.80, Cc, Z = 4 in a cell of dimensions a = 27.9984(9) Å, b = 9.7494(3) Å, c= 28.6619(9) Å, β = 96.636(2)°, V = 7771.4(4) Å^3, D_{alc} = 1.397 Mg/m^3, F(000) = 3368. The structure was refined on F^2 to R_w = 0.1894, conventional R = 0.0651 (10631 reflections with $I > 2\sigma(I)$), and a goodness of fit = 1.056 for 989 refined parameters.

There are three distinct moieties in the asymmetric unit, the rotaxane thread, the rotaxane macrocycle, and 4 molecules of chloroform. The crystal structure solved and refined readily in space group Cc. Efforts were made to solve and refine the structure in centrosymmetric C2/c. The thread portion of the rotaxane structure behaves well in this space group, but the macrocycle suffers from a great deal of disorder. On this basis, space group Cc was chosen. The symmetry-checking routine of PLATON (Spek, 2004), ADDSYM, shows a 91% fit of the atom positions to C2/c. When the EXACT option is run, no higher symmetry is suggested. In Cc, some disorder remains. It is notable that the thread is free of disorder. The macrocycle shows disorder in the benzylic carbon C46, with site occupancy 0.64(2) for the major position. There is also disorder at C69, site occupancy 0.47(4) for C69 and 0.53(4) for C69'. Disorder is also present at the solvent positions. Chloroform molecules C1s and C4s exhibit no disorder. Molecule C2s shows disorder in the positions for Cl4 and Cl5, site occupancy factors 0.81(4) and 0.55(4) for the major sites. Molecule C3s is disordered at Cl8 and Cl9, with site occupancy factors 0.52(4) and 0.61(7). Hydrogens were added at calculated geometries and set to ride on the position of the parent atom. Thermal parameters were set to 1.2 times the equivalent isotropic U of the parent atom. All non-hydrogen atoms were refined with anisotropic parameters for thermal motion. The largest peaks in the final difference map, 1.43-0.97 e$^-$/Å^3, may be remnants of unmodeled disorder.

Pyridyl-containing rotaxane 3

Single crystal was obtained from the slow diffusion of cyclohexane into a solution of **3** in chloroform. Crystallographic summary: triclinic, $C_{74}H_{66}N_8O_8$, M_r = 1195.35, $P\bar{1}$, Z = 1 in a cell of dimensions a = 9.7987(1) Å, b = 10.9613(2) Å, c= 14.4900(2) Å, α = 86.839(1)°, β = 78.258(1)°, γ= 77.305(1)°, V = 1486.41(4) Å^3, D_{alc} = 1.335 Mg/m^3, F(000) = 630. The structure was refined on F^2 to R_w = 0.1188, conventional R = 0.0438 (8035 reflections with $I > 2\sigma(I)$), and a goodness of fit = 1.027 for 422 refined parameters.

The asymmetric unit contains one-half thread, one-half macrocycle, and one molecule of water. The complete structure is generated by inversion through (1-x, 2-y, 2-z). The assembly forms a linear chain linked by water molecules bridging O2 and O3 of neighboring rotaxanes. This chain propagates parallel to the b-axis. The threads are perpendicular to the b-axis. The squaraine thread oxygens are hydrogen-bonded to hydrogens H2N and H4N of the macrocycles. Hydrogens bound to nitrogen and the hydrogens of the water molecule were located by difference electron density map and freely refined in subsequent cycles of least-squares refinement. A parameter for isotropic thermal motion was refined for each of these hydrogens. All other hydrogens were placed at calculated geometries and allowed to ride on the position of the parent atom.

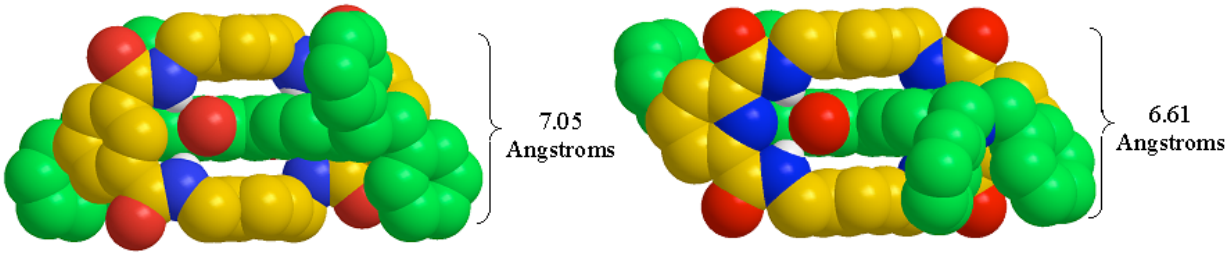


Figure S5: Space-filling models of isophthalamide rotaxane **2** (left) and pyridyl rotaxane **3** (right) illustrating centroid to centroid distance between macrocycle xylylene units. The major occupancy structure of **2** is shown.

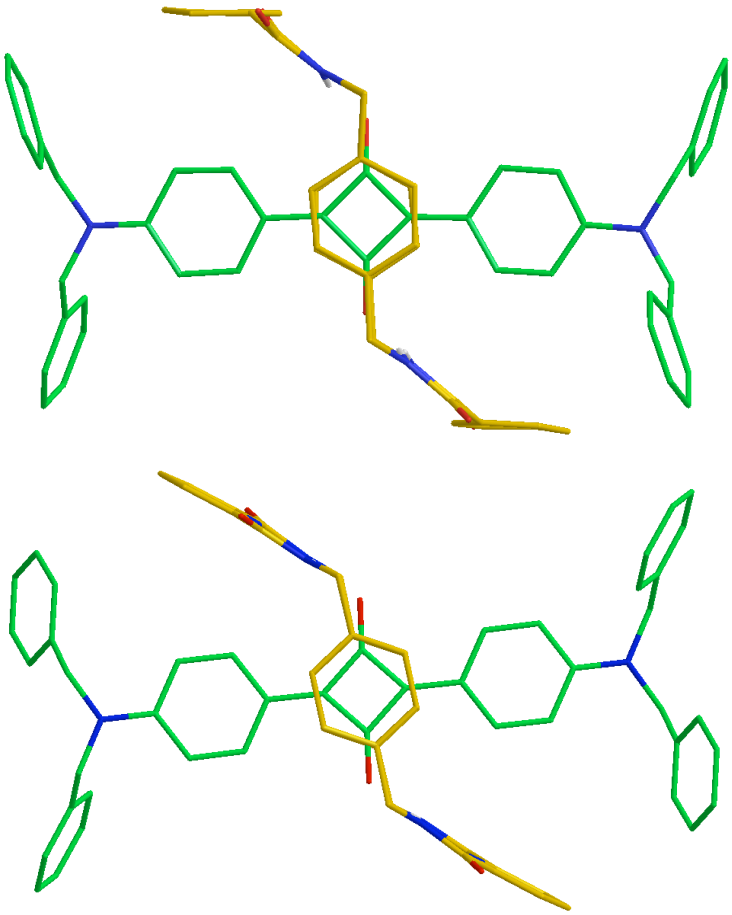


Figure S6: Side projections of isophthalamide rotaxane **2** (top) and pyridyl rotaxane **3** (bottom). The major occupancy structure of **2** is shown.

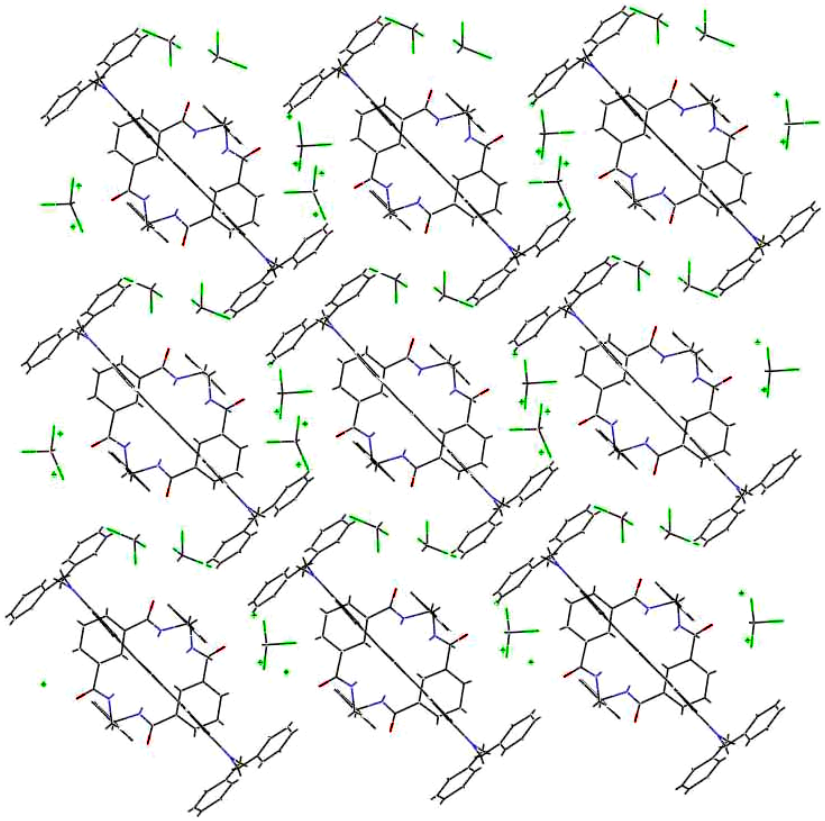


Figure S7: Crystal packing of (**2**•4$CHCl_3$).

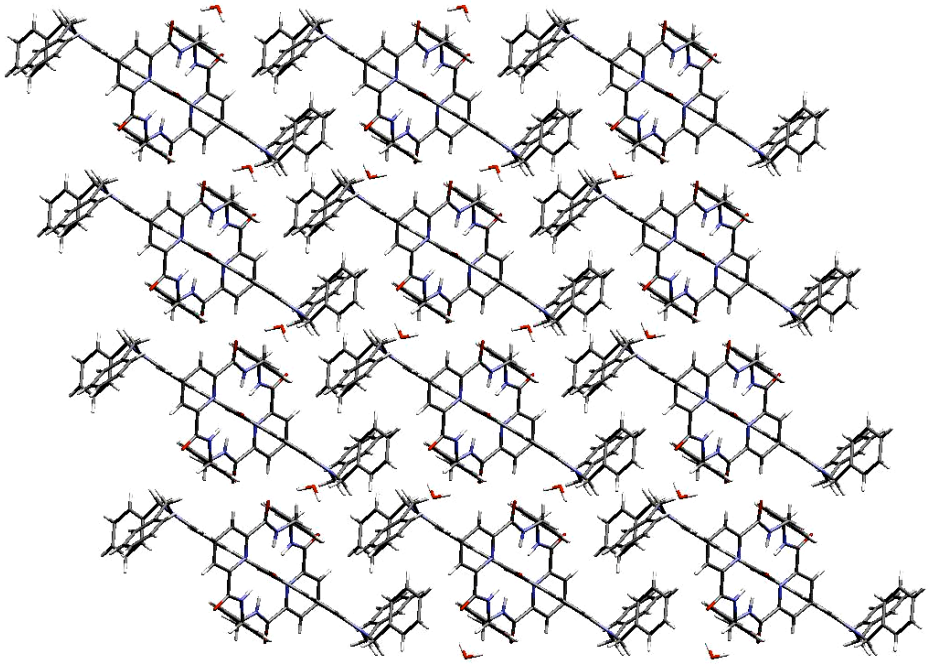


Figure S8: Crystal packing of (**3**•2H_2O).