Supporting Information

Diaminotriazine substituted diphenyl ether: Reversible structural transformation and solvent dependent solid state fluorescence

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General procedure for the Cyanophenoxy-benzonitrile (a–e) preparation: Fluorobenzonitrile (10 mmol), hydroxy benzonitrile (10~12 mmol) and potassium carbonate (20 mmol) were added to 30 ml of dimethyl sulfoxide (DMSO). Appling microwave power 300 W rises the DMSO temperature from room temperature to boiling point within 30–40 s and then the solution was held boiling for 10 min. After completion of the reaction, it was cooled to room temperature, put into ice water and stirred for 30 min to precipitate the product. Filtration of the precipitation followed by washing with water afforded the desired products (85 %).

2-(2'-cyanophenoxy)benzonitrile (a): It was prepared from 2-hydroxy benzonitrile and 2-fluorobenzonitrile: ^{1}H: 7.73, d, 2H, 7.54, t, 2H, 7.36, d, t, 2H, 7.00, d, 1H; ^{13}C: 157.8, 134.6, 132.3, 121.4, 119.5, 117.3, 106.9.

2-(3'-cyanophenoxy)benzonitrile (b): It was prepared from 3-hydroxy benzonitrile and 2-fluorobenzonitrile: ^{1}H: 7.73, d, 1H, 7.54-7.60, m, 3H, 7.28-7.36, m, 3H, 7.00, d, 1H; ^{13}C: 157.4, 155.6, 134.2, 133.9, 130.7, 127.8, 124.1, 123.5, 121.8, 118.1, 117.3, 114.9, 113.6, 104.6.

2-(4'-cyanophenoxy)benzonitrile (c): It was prepared from 2-hydroxy benzonitrile and 4-fluorobenzonitrile: ^{1}H: 7.74, d, 1H, 7.71, d, 2H, 7.62, t, 1H, 7.34, t, 1H, 7.14, d, 2H,

7.10, d,1H; ^{13}C: 159.0, 156.6, 134.2, 134.0, 133.8, 124.6, 119.2, 118.8, 117.8, 114.8, 107.5, 105.2.

3-(4'-cyanophenoxy)benzonitrile (d): It was prepared from 3-hydroxy benzonitrile and 4-fluorobenzonitrile: ^{1}H: 7.69, d, 2H, 7.51-7.54, m, 2H, 7.30-7.37, m, 1H, 7.28, s, 1H, 7.10, d, 2H; ^{13}C: 160.0, 154.8, 133.5, 130.6, 127.7, 123.6, 122.1, 118.0, 117.8, 117.6, 113.5, 107.0.

4-(4'-cyanophenoxy)benzonitrile (e): It was prepared from 4-hydroxy benzonitrile and 4-fluorobenzonitrile: ^{1}H: 7.72, d, 2H; 7.12, d, 2H; ^{13}C: 158.8, 133.6, 119.2, 117.4, 107.9.

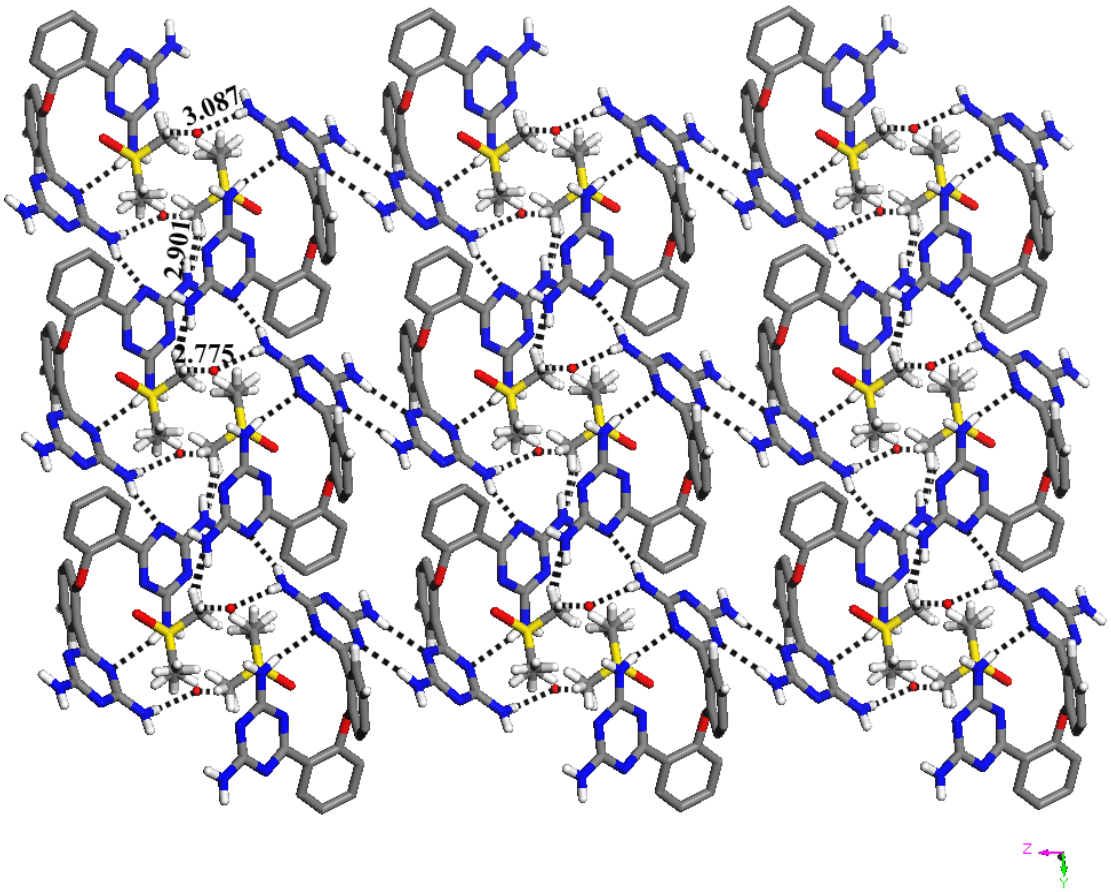


Figure S1. Crystal packing of 1. Only H atoms in the amines are shown; C (grey), N (blue), O (red), S (yellow) H (white); H-bonds (broken line). Methyl hydrogen atoms of DMSO are disordered in the crystal lattice. H-bonds (broken line). $d_{D\cdots A}$ distances (Å) are marked.

Table S1. H-bond table

	N–H···N	**N–H···O**	**O–H···N**	**C–H···N**	**C–H···O**	**C–H···S**
1	2.04 3.05(9) 176 2.51 3.25(9) 130 2.12 3.12(5) 169 2.15 3.14(4) 167 2.06 3.06(2) 166	2.04 2.99(7) 156		2.72 3.75(1) 156 2.73 3.54(5) 132 2.57 3.48(3) 140		
3a	2.16 3.15(1) 163 1.95 2.97(3) 175	2.13 3.10(2) 158		2.62 3.58(9) 148 2.66 3.73(2) 167 2.09 2.90(6) 129 2.06 2.90(6) 133	2.71 3.62(5) 140 1.83 2.79(1) 143 2.01 2.79(1) 125	2.55 3.62(1) 164
3b	2.06 3.08(1) 179 2.30 3.16(1) 141 2.04 3.05(8) 173 2.03 3.01(1) 162	2.25 3.12(1) 142 2.40 3.37(7) 161 2.07 2.96(1) 145	1.86 2.84(1) 167 2.30 3.16(3) 146	2.25 3.29(5) 162	2.51 3.55(7) 162 2.27 3.35(1) 168	
3c	2.23 3.19(6) 159 2.71 3.52(5) 137 2.06 3.06(4) 171 2.10 3.10(5) 173 2.10 3.10(9) 168 2.01 3.02(5) 178			2.68 3.61(5) 144 2.55 3.62(5) 170 2.65 3.44(1) 128		
5	2.03 3.02(9) 164 2.04 3.06(1) 174 2.04 3.04(9) 170 2.04 3.05(1) 171	1.99 2.95(7) 159 2.12 2.85(5) 128	1.87 2.84(4) 167	2.63 3.54(8) 142 2.64 3.53(2) 138	2.47 3.38(2) 140	

The columns are in the order, H···A, D···A (Å) and D-H···A angle (^{o})

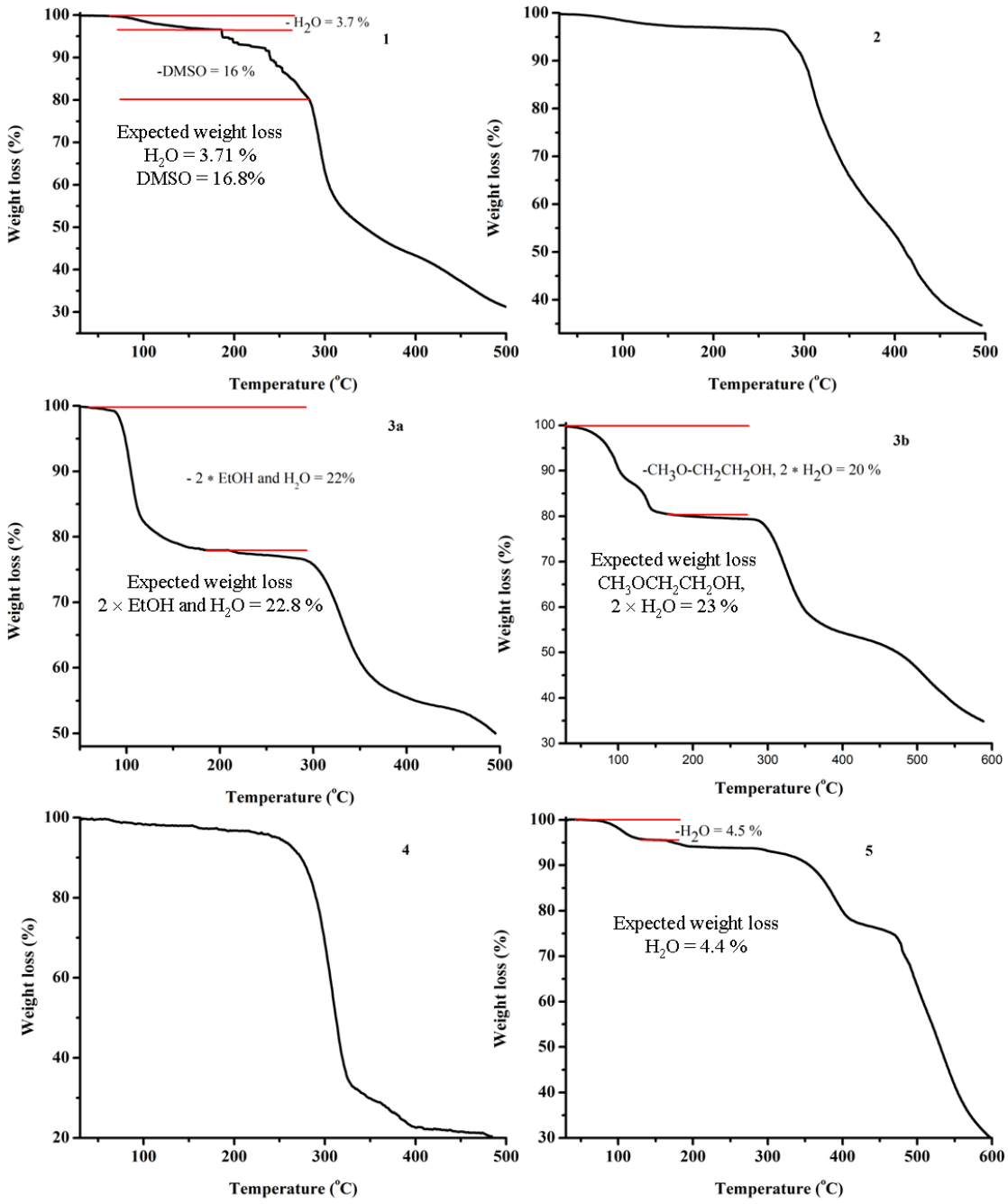


Figure S2. Thermo-gravimetric analysis.

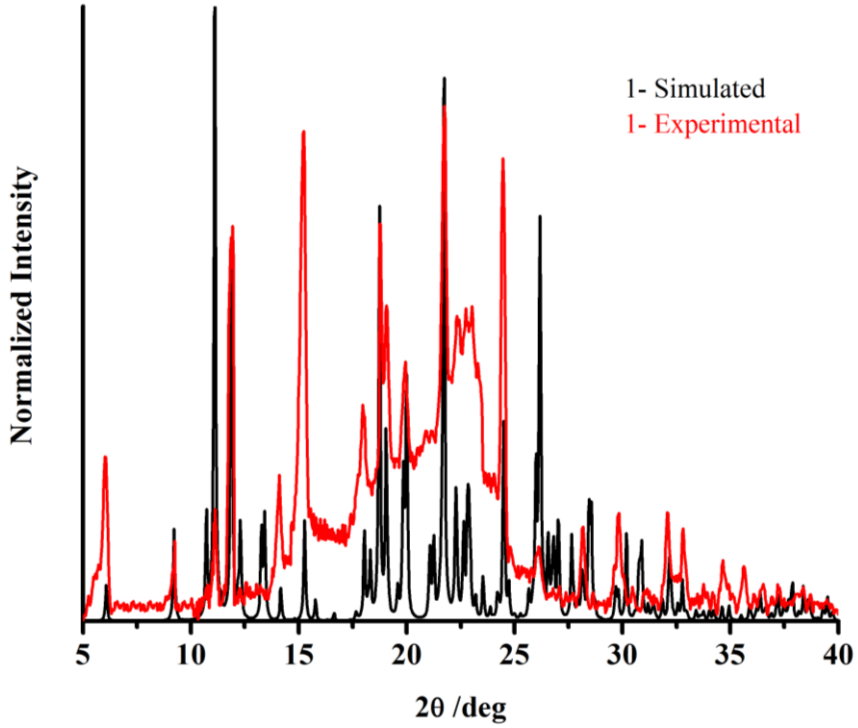
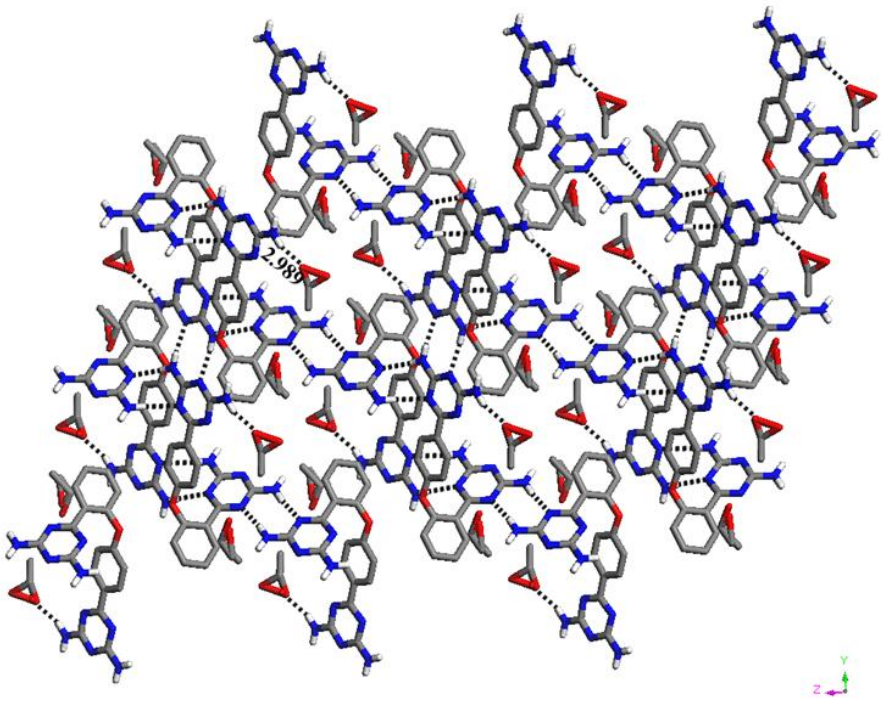
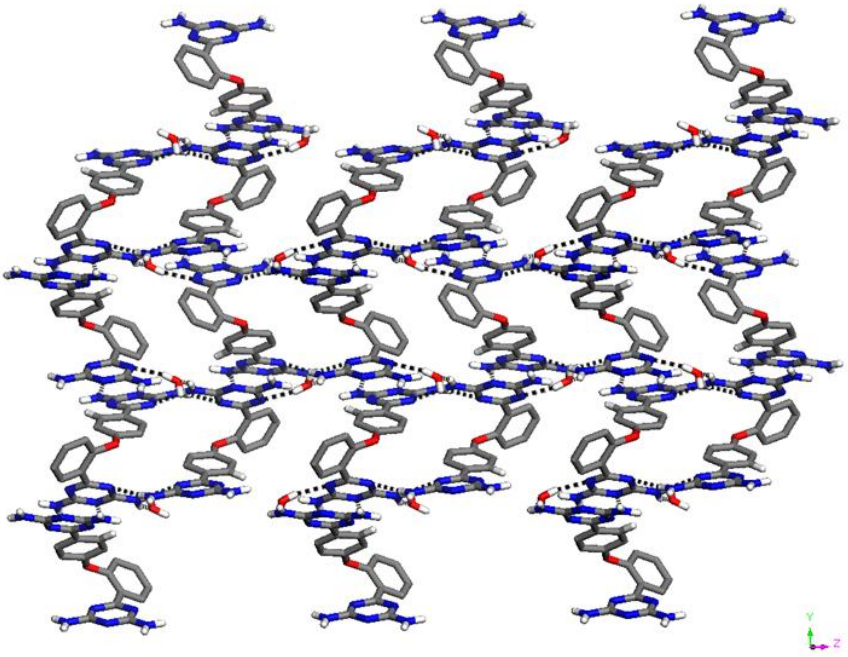


Figure S3. PXRD patterns of 1

(a)



(b)



(c)

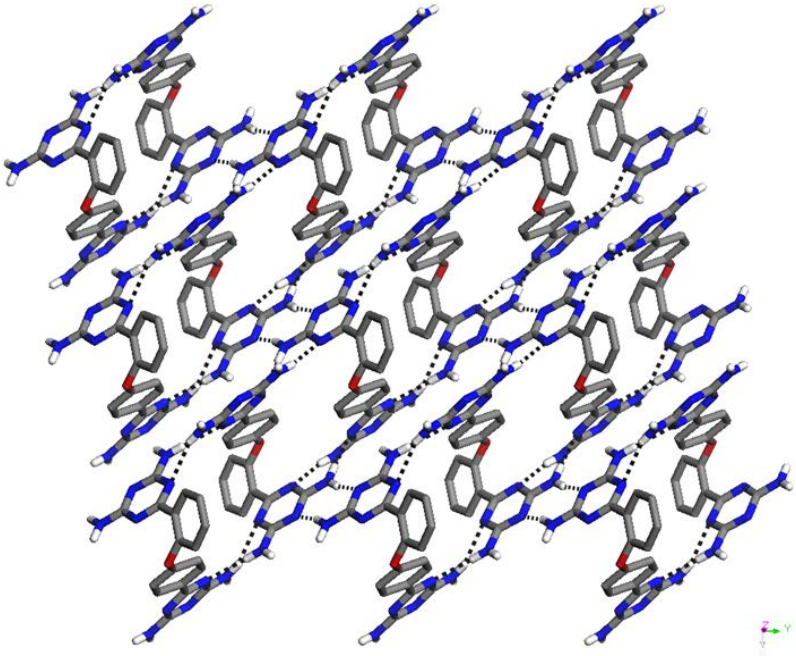


Figure S4. Crystal packing of 3a (a), 3b (b) and 3c (c). Only H atoms in the amines are shown; C (grey), N (blue), O (red), H (white); H-bonds (broken line). Ethanol oxygens are disordered in the crystal lattice of *O, P*-3a. H-bonds (broken line). $d_{D\cdots A}$ distances (Å) are marked.

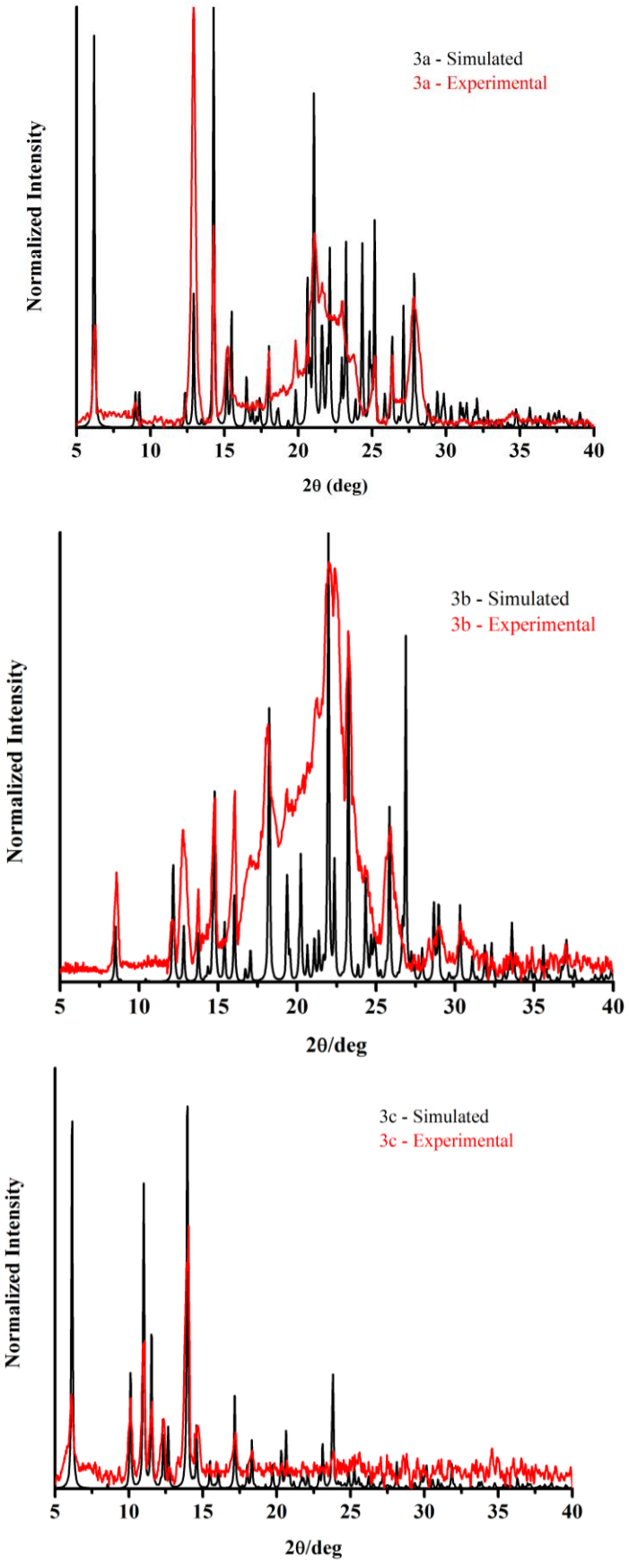
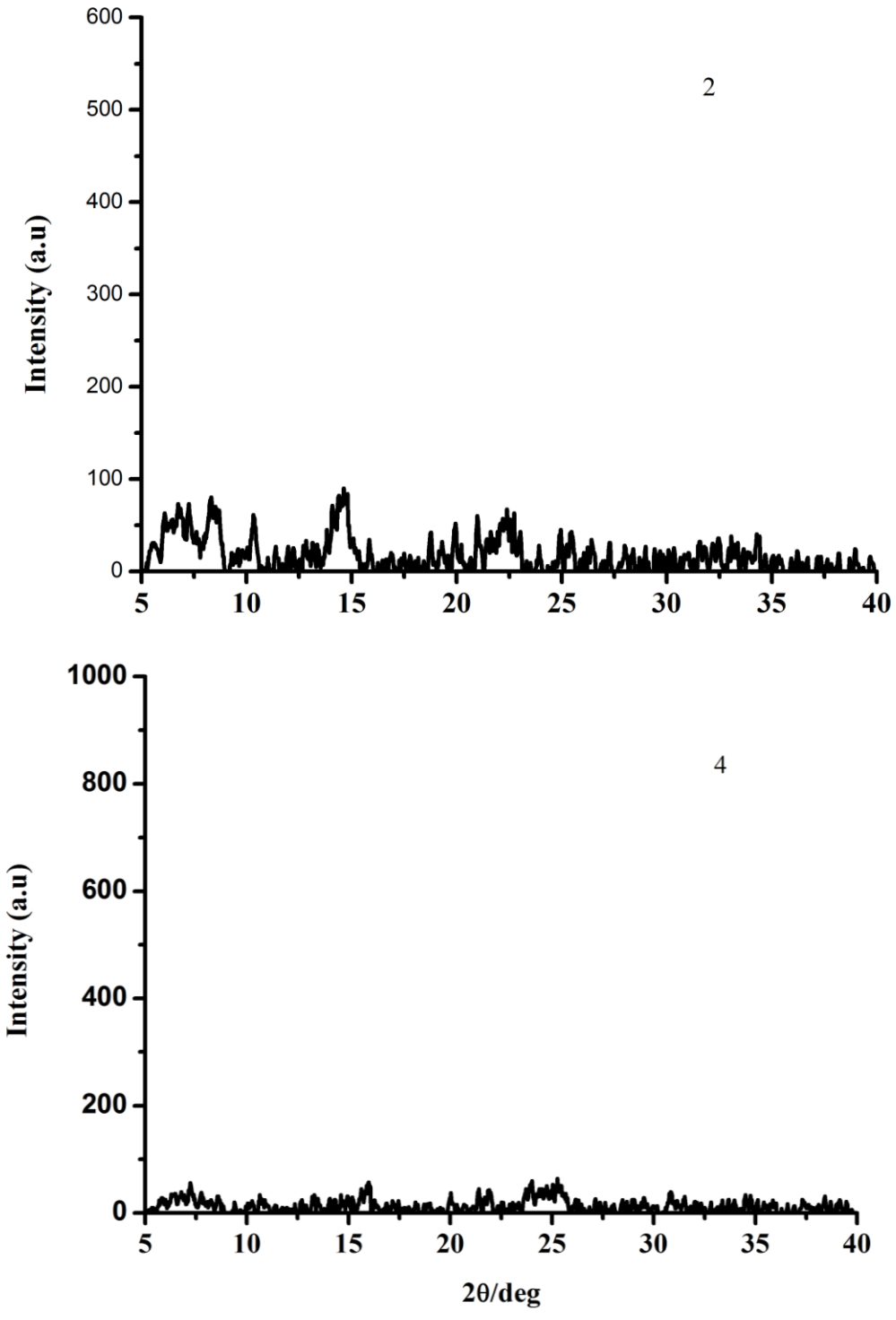


Figure S5. PXRD patterns of 3.



S6. PXRD patterns of 2 and 4.

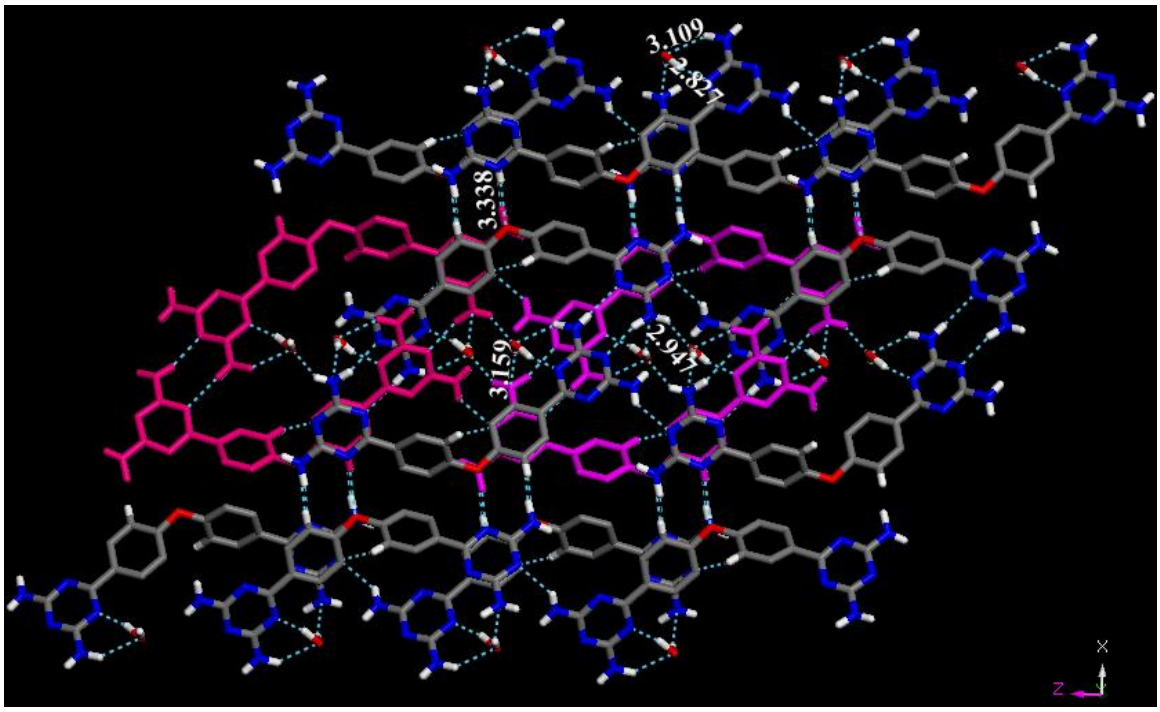


Figure S7. Crystal packing of 5. Only H atoms in the amines are shown; C (grey), N (blue), O (red), H (white); H-bonds (broken line). Pink and orange colored molecules show the opposite helices in the crystal lattice. H-bonds (broken line). $d_{D\cdots A}$ distances (Å) are marked.

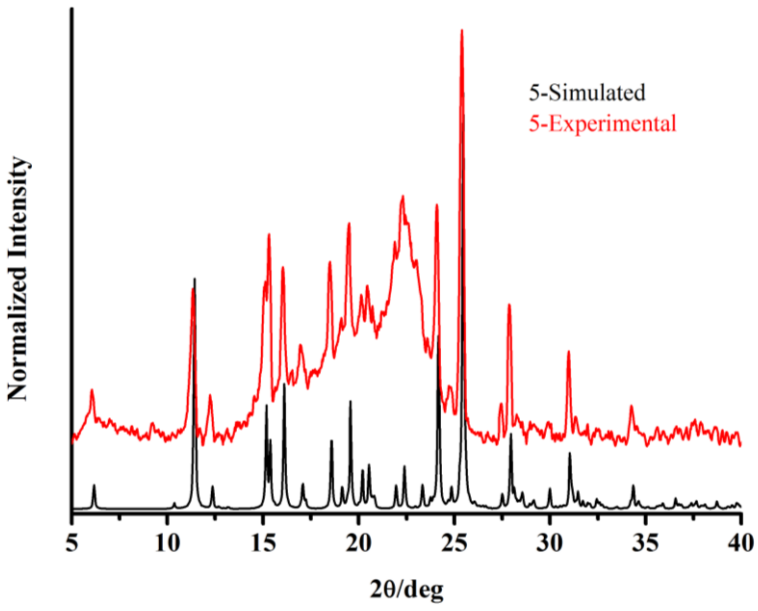


Figure S8. PXRD patterns.

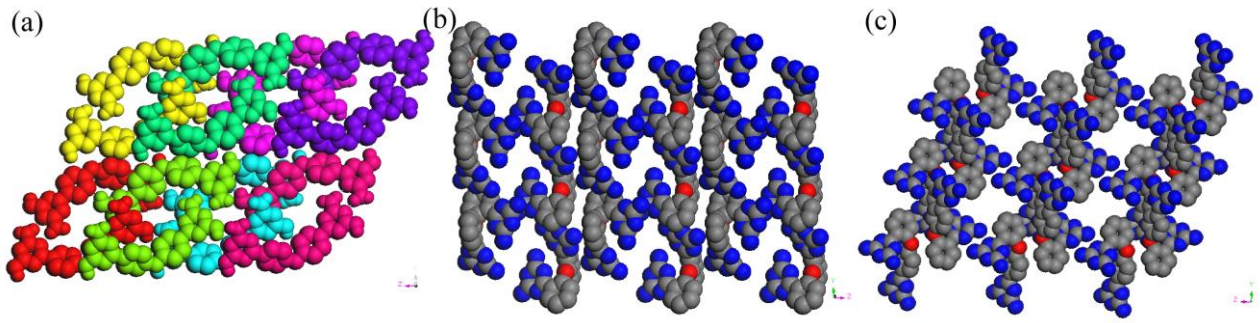


Figure S9. Space-filling crystal packing of (a) 5, (b) 1, and (c) 3b.

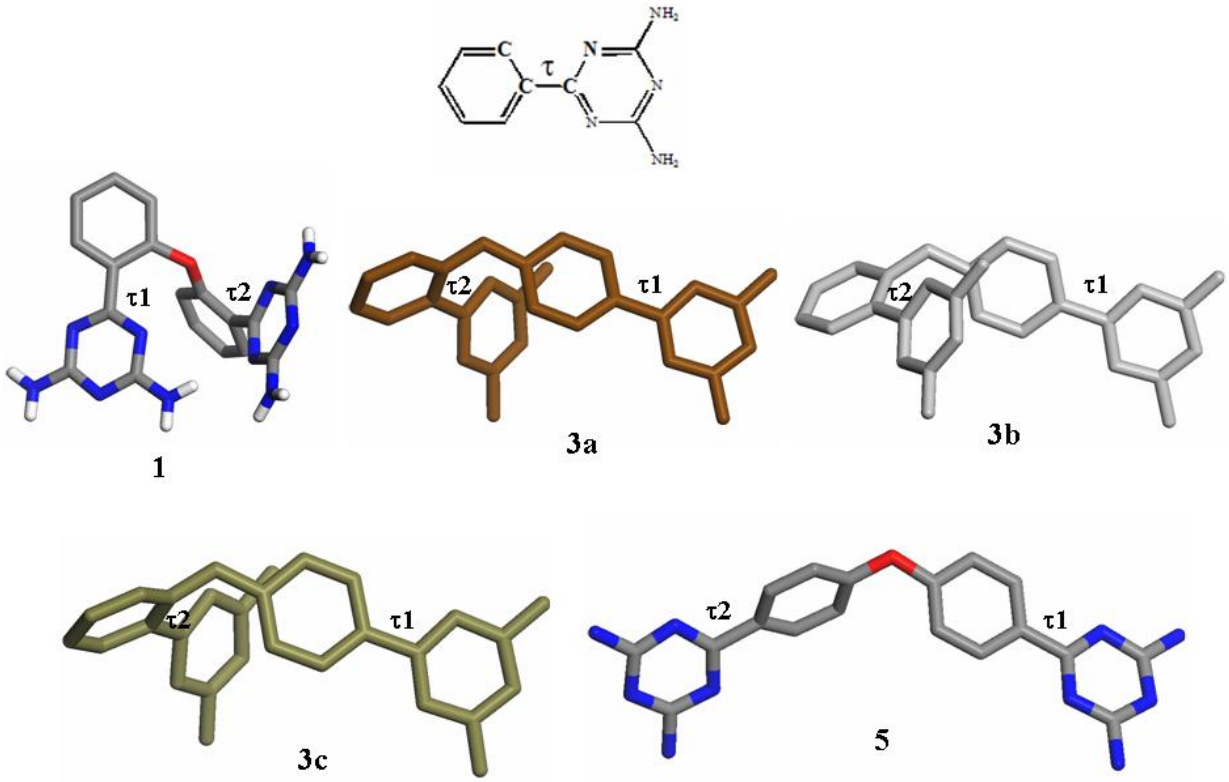


Figure S10. The molecular twist of diaminotriazine in 1, 3 and 5 defined by torsional angle (τ).

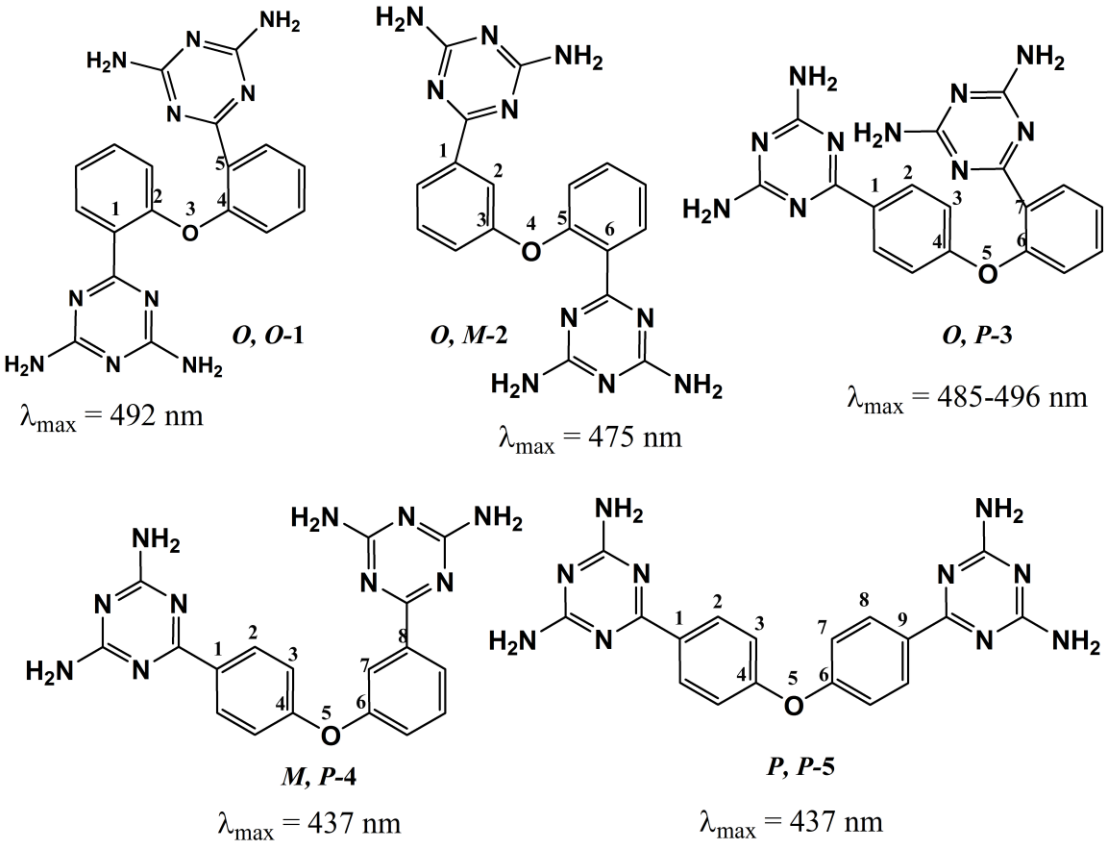


Figure S10. Molecular structure with numbering between diaminotriazine and fluorescence maximum.