Electronic Supplementary Material (ESI)

Encapsulation of Stilbazolium-type Dyes into Layered Metal–Organic Frameworks: Solvent-Dependent Luminescence Chromisms and Their Mechanisms

Li-Ming Zhao, Xia-Qiang Shen, Li-Ting Tan, Wen-Ting Zhang, Kai-Yue Song, Rong Jiang, Hao-Hong Li*, Zhi-Rong Chen*

College of chemistry, Fuzhou University, Fuzhou, Fujian, 350116, *China*.

Supporting information

Computation Methods

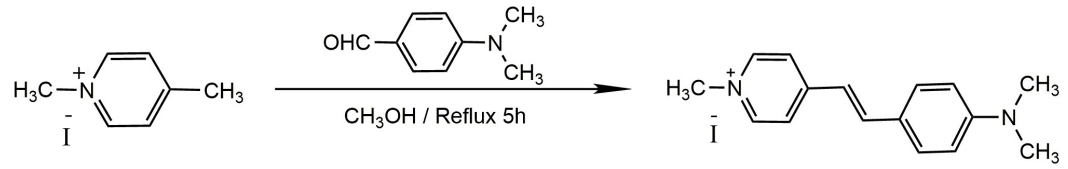
In the theoretical simulation of dye@Cd-MOCs system, the Vienna ab initio simulation package (VASP) program based on density functional theory (DFT) methods and plane wave basis set was adopted.[1] The exchange−correlation functions were treated by the Perdew−Burke−Ernzerhof (PBE)[2] and PAW pseudopotential basis set.[3,4] The dye@Cd-MOCs composites were fully optimized taking the spin polarization into account. The plane-wave basis set with a cutoff energy of 400 eV. The accuracy in the energy convergence and force field are 10^{-2}eV and 0.5 eV. The Brillouin-zone integration was performed on a grid of 1×1×1 Monkhorst−Pack special K-points. The models of $Cd(BA)_3$(Solvent) were calculated using Gaussian 09 program package,[5] in which 6-31g basis set was applied on C, H, O, N, and pseudopotential basis set lanl2dz was adopted on Cd. The calculations were performed by using spin restricted DFT wave functions B3LYP.

Synthesis of Stilbazolium-type Dyes

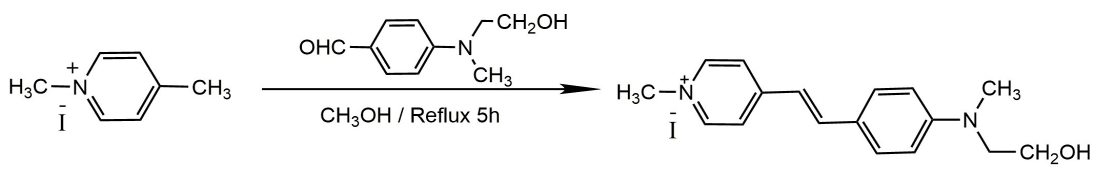
Synthesis of 4'-dimethylamino-N-methyl stilbazolium iodide (DAST)·I: The synthesis routes of three organic dyse can be seen in Scheme S1. 1,4-dimethylpyridin-1-ium iodide (1.4200 g, 10 mmol) and 4-*N,N*-dimethylamino-benzaldehyde (0.1490 g, 10 mmol) were mixed in 30mL ethanol in a round flask, then the mixture was refluxed for 5 hours using piperidine (5 drops) as catalyst. The product was washed with ethanol for three times.1H NMR (400 MHz, DMSO) δ 8.70 (d, J = 6.4 Hz, 2H), 8.07 (d, J = 6.5 Hz, 2H), 7.93 (d, J = 16.1 Hz, 1H), 7.61 (d, J = 8.7 Hz, 2H), 7.19 (d, J = 16.1 Hz, 1H), 6.78 (d, J = 8.7 Hz, 2H), 4.19 (s, 3H), 3.02 (s, 6H).

Synthesis of 4-[(4-N-methyl-N-hydroxyethylamino)styryl]-1-methylpyridiniumiodide (HMAS)·I: N-methyl-N-hydroxyethyl-4-aminobenzaldehyde (0.179 g, 0.1 mol) and 1,4-dimethylpyridinium iodide (0.235 g, 0.1 mol) were mixed in ethanol (30 mL), then the mixture was removed into flask and refluxed for 5 hours under 80°C. The product was obtained after washing by ethanol and drying in vacuum desiccator. 1H NMR (400 MHz, DMSO) δ 8.69 (d, J = 5.8 Hz, 2H), 8.05 (d, J = 5.8 Hz, 2H), 7.92 (d, J = 16.0 Hz, 1H), 7.59 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 16.0 Hz, 1H), 6.80 (d, J = 8.2 Hz, 2H), 4.77 (s, 1H), 4.19 (s, 3H), 3.59 (s, 2H), 3.51 (s, 2H), 3.04 (s, 3H).

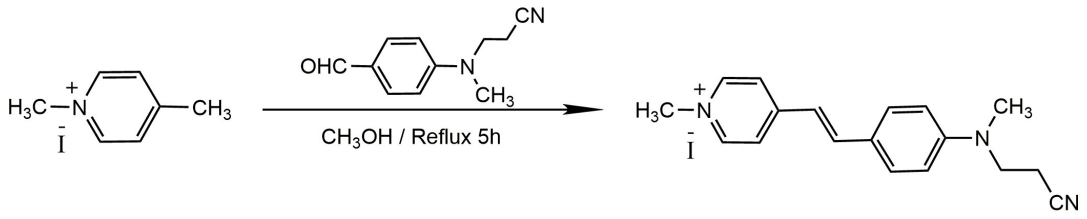
Synthesis of 4'-(4-(2-cyanoethyl)(methyl)amino)-N-methyl stilbazolium iodide (CMAS)·I: The synthesis of (CMAS)·I was the same with (HMAS)·I except that N-methyl-N-hydroxyethyl-4-aminobenzaldehyde (0.179 g, 0.1 mol) was used as starting material. 1H NMR (400 MHz, DMSO) δ 8.72 (d, J = 6.6 Hz, 2H), 8.09 (d, J = 6.7 Hz, 1H), 7.94 (d, J = 16.1 Hz, 1H), 7.62 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 16.2 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 4.20 (s, 3H), 3.79 (t, J = 6.6 Hz, 2H), 3.05 (s, 3H), 2.78 (t, J = 6.6 Hz, 2H).



(a)



(b)



(c)

Scheme S1 Synthesis route of three dyes: (a) (DAST)·I; (b) (HMAS)]·I and (c) (CMAS)·I

Table S1 Selected bond lengths (Å) and angles (°) of 1-1 and 1-2

1-1					
Cd(1)-O(1)	2.338(5)	Cd(1)-O(2)	2.369(4)	Cd(1)-O(3)#1	2.159(5)
Cd(1)-O(5)#2	2.304(5)	Cd(1)-O(6)#2	2.356(5)	Cd(1)-O(8)	2.307(8)
Cd(2)-O(2)	2.314(4)	Cd(2)-O(2)#4	2.314(4)	Cd(2)-O(4)#1	2.243(4)
Cd(2)-O(4)#3	2.243(4)	Cd(2)-O(7)	2.258(5)	Cd(2)-O(7)#4	2.258(5)
O(3)#1-Cd(1)-O(8)	92.7(3)	O(5)#2-Cd(1)-O(8)	89.5(3)	O(8)-Cd(1)-O(1)	90.8(2)
O(8)-Cd(1)-O(6)#2	87.3(3)	O(3)#1-Cd(1)-O(2)	103.63(18)	O(5)#2-Cd(1)-O(2)	118.3(2)
O(8)-Cd(1)-O(2)	145.8(2)	O(1)-Cd(1)-O(2)	55.38(16)	O(6)#2-Cd(1)-O(2)	92.63(19)
O(4)#1-Cd(2)-O(2)	90.48(17)	O(4)#3-Cd(2)-O(2)	89.52(17)	O(7)-Cd(2)-O(2)	85.6(2)
O(7)#4-Cd(2)-O(2)	94.4(2)	O(4)#1-Cd(2)-O(2)#4	89.52(17)	O(4)#3-Cd(2)-O(2)#4	90.48(17)
O(7)-Cd(2)-O(2)#4	94.4(2)	O(7)#4-Cd(2)-O(2)#4	85.6(2)	O(2)-Cd(2)-O(2)#4	180.0
Symmetry codes: #1 x,y-1,z+1; #2 x-1,y,z+1; #3 -x+1,-y+1,-z; #4 -x+1,-y,-z+1					
1-2					
Cd(1)-O(1)	2.299(4)	Cd(1)-O(2)	2.453(4)	Cd(1)-O(3)#2	2.332(4)
Cd(1)-O(4)#2	2.353(4)	Cd(1)-O(5)#1	2.171(4)	Cd(1)-O(8)	2.303(5)
Cd(2)-O(1)	2.301(4)	Cd(2)-O(1)#4	2.301(4)	Cd(2)-O(6)#3	2.243(4)
Cd(2)-O(6)#1	2.243(4)	Cd(2)-O(7)#4	2.264(4)	Cd(2)-O(7)	2.264(4)
O(5)#1-Cd(1)-O(8)	94.71(19)	O(5)#1-Cd(1)-O(3)#2	91.46(16)	O(8)-Cd(1)-O(3)#2	87.75(18)
O(1)-Cd(1)-O(4)#2	91.41(15)	O(8)-Cd(1)-O(4)#2	86.8(2)	O(3)#2-Cd(1)-O(4)#2	55.70(16)
O(1)-Cd(1)-O(2)	54.92(14)	O(8)-Cd(1)-O(2)	84.34(16)	O(6)#3-Cd(2)-O(7)#4	87.10(16)
O(6)#1-Cd(2)-O(7)#4	92.90(16)	O(6)#3-Cd(2)-O(7)	92.90(16)	O(6)#1-Cd(2)-O(7)	87.10(16)
O(7)#4-Cd(2)-O(7)	180.000(1)	O(7)#4-Cd(2)-O(1)	97.41(17)	O(7)-Cd(2)-O(1)	82.59(17)
O(7)#4-Cd(2)-O(1)#4	82.59(17)	O(7)-Cd(2)-O(1)#4	97.41(17)		
Symmetry codes: #1 x,y+1,z-1; #2 x+1,y,z-1; #3 -x+1,-y,-z+2; #4 -x+1,-y+1,-z+1					

Table S2 Selected bond lengths (Å) and angles (°) of 1-3 and 2

1-3					
Cd(1)-O(2)	2.239(3)	Cd(1)-O(2)#1	2.239(3)	Cd(1)-O(3)#2	2.306(4)
Cd(1)-O(3)#3	2.306(4)	Cd(1)-O(7)	2.275(4)	Cd(1)-O(7)#1	2.275(4)
Cd(2)-O(1)	2.160(4)	Cd(2)-O(6)#4	2.337(5)	Cd(2)-O(3)#2	2.304(3)
Cd(2)-O(4)#2	2.451(4)	Cd(2)-O(5)#4	2.346(4)	Cd(2)-O(8)	2.304(5)
O(2)#1-Cd(1)-O(7)	92.35(16)	O(2)-Cd(1)-O(7)	87.65(16)	O(2)#1-Cd(1)-O(7)#1	87.65(16)
O(2)-Cd(1)-O(7)#1	92.35(16)	O(7)-Cd(1)-O(7)#1	180.000(1)	O(7)-Cd(1)-O(3)#2	83.09(16)
O(7)#1-Cd(1)-O(3)#2	96.91(16)	O(7)-Cd(1)-O(3)#3	96.91(16)	O(7)#1-Cd(1)-O(3)#3	83.09(16)

O(1)-Cd(2)-O(6)#4	93.38(17)	O(8)-Cd(2)-O(6)#4	88.80(19)	O(3)#2-Cd(2)-O(6)#4	125.07(16)
O(8)-Cd(2)-O(5)#4	88.2(2)	O(3)#2-Cd(2)-O(5)#4	91.42(14)	O(6)#4-Cd(2)-O(5)#4	55.24(17)
O(1)-Cd(2)-O(4)#2	106.22(17)	O(8)-Cd(2)-O(4)#2	84.64(18)	O(3)#2-Cd(2)-O(4)#2	54.30(14)
Symmetry codes: #1 -x+1,-y,-z+2; #2 x,y-1,z+1; #3 -x+1,-y+1,-z+1; #4 x+1,y-1,z					
2					
Cd(1)-O(1)	2.472(5)	Cd(1)-O(2)	2.362(4)	Cd(1)-O(3)#1	2.378(7)
Cd(1)-O(4)#1	2.240(6)	Cd(1)-O(6)#2	2.241(4)	Cd(1)-O(7)	2.271(6)
Cd(1)-O(8)	2.662	Cd(2)-O(2)	2.282(4)	Cd(2)-O(2)#4	2.282(4)
Cd(2)-O(5)#3	2.178(4)	Cd(2)-O(5)#2	2.178(4)	Cd(2)-O(8)#4	2.367(4)
Cd(2)-O(8)	2.367(4)	O(6)#2-Cd(1)-O(7)	83.5(2)	O(6)#2-Cd(1)-O(2)	95.70(15)
O(7)-Cd(1)-O(3)#1	92.3(4)	O(4)#1-Cd(1)-O(3)#1	50.7(2)	O(6)#2-Cd(1)-O(3)#1	86.7(2)
O(4)#1-Cd(1)-O(1)	78.7(2)	O(7)-Cd(1)-O(1)	91.7(2)	O(2)-Cd(1)-O(1)	53.16(15)
O(5)#3-Cd(2)-O(8)#4	93.65(15)	O(5)#2-Cd(2)-O(8)#4	86.35(15)	O(2)-Cd(2)-O(8)#4	99.09(18)
O(2)#4-Cd(2)-O(8)#4	80.91(18)	O(5)#3-Cd(2)-O(8)	86.35(15)	O(5)#2-Cd(2)-O(8)	93.65(15)
O(2)-Cd(2)-O(8)	80.91(18)	O(2)#4-Cd(2)-O(8)	99.09(18)	O(8)#4-Cd(2)-O(8)	180.0
Symmetry codes: #1 x+1/2,y-1/2,z; #2 x+1/2,y+1/2,z; #3 -x,-y,-z+1; #4 -x+1/2,-y+1/2,-z+1					

Table S3 Hydrogen bridging details of this work

Compound	D–H···A	D–H/Å	H···A/Å	D···A/Å	∠(D–H···A)/º	Symmetry codes
1-1	C(29)-H(29A)···O(7)	0.97	2.56	2.89(4)	100	
	C(31)-H(31B)···O(1)	0.97	2.53	3.45(3)	159	-1+x,y,z
	C(36)-H(36A)···O(8)	0.97	2.26	2.72(2)	108	
1-2	C(10)-H(10)···O(9)	0.93	2.55	3.416(9)	154	x,-1+y,1+z
	C(20)-H(20)···O(9)	0.93	2.46	3.300(11)	151	x,-1+y,1+z
	C(29)-H(29C)···O(6)	0.96	2.56	3.26(3)	130	1-x,-y,2-z
	C(30)-H(30C)···O(3)	0.96	2.37	3.228(11)	149	1+x,y,-1+z
	C(35)--H(35C)···O(4)	0.96	2.41	3.283(17)	151	1+x,y,-1+z
1-3	C(5)-H(5)···O(9)	0.93	2.59	3.44(2)	153	
	C(29)-H(29A)···O(2)	0.96	2.25	3.155(19)	156	1-x,-y,2-z
	C(31)-H(31C)···O(6)	0.96	2.38	3.238(11)	149	1+x,-1+y,z
	C(34)-H(34C)···O(5)	0.96	2.37	3.26(2)	154	1+x,-1+y,z
2	C(30)-H(30B)···N(3)	0.96	2.59	3.44(5)	149	-x,y,3/2-z
	C(32)-H(32B)···O(1)	0.96	2.47	3.23(2)	136	x,-y,-1/2+z
	C(34)-H(34)···O(1)	0.93	2.55	3.44(3)	159	-1/2+x,1/2+y,z

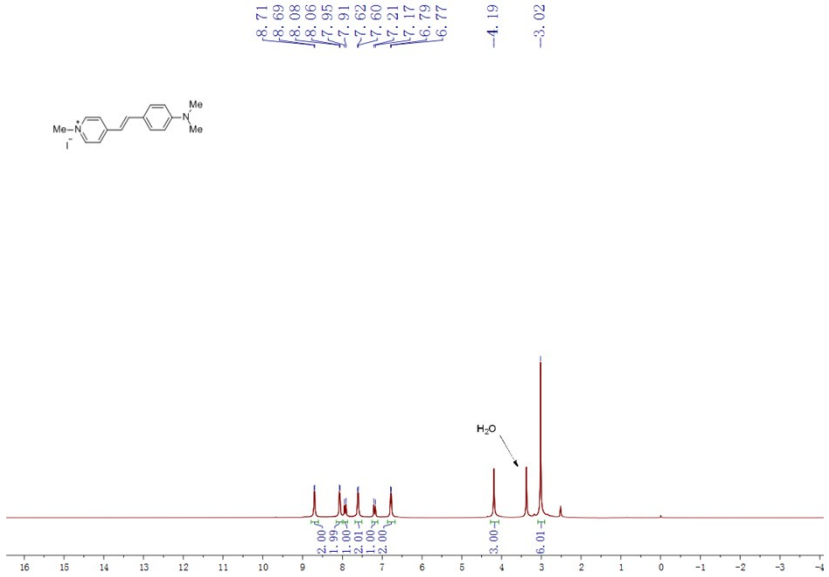
Table S4 π–π stacking interactions in this work (lengths in Å and angles in °)

Compound	**Cg(I)···Cg(J)**	**Symmetry code**	**Dist. Centroids**	**Dihedral angle**	**CgI_Perp dist.**	**CgJ_Perp dist.**
1-1	Cg(1)→Cg(1)#1	2-x,1-y,-z	3.634(4)	0	3.624(2)	3.625(2)
	Ring Cg(1): C(7)→C(8)→C(9)→C(10)→C(11)→C(12)→					
1-2	Cg(1)→Cg(1)#1	-x,-y,2-z	3.646(3)	0	3.622(2)	3.623(2)
	Ring Cg(1): C(7)→C(8)→C(9)→C(10)→C(11)→C(12)→					

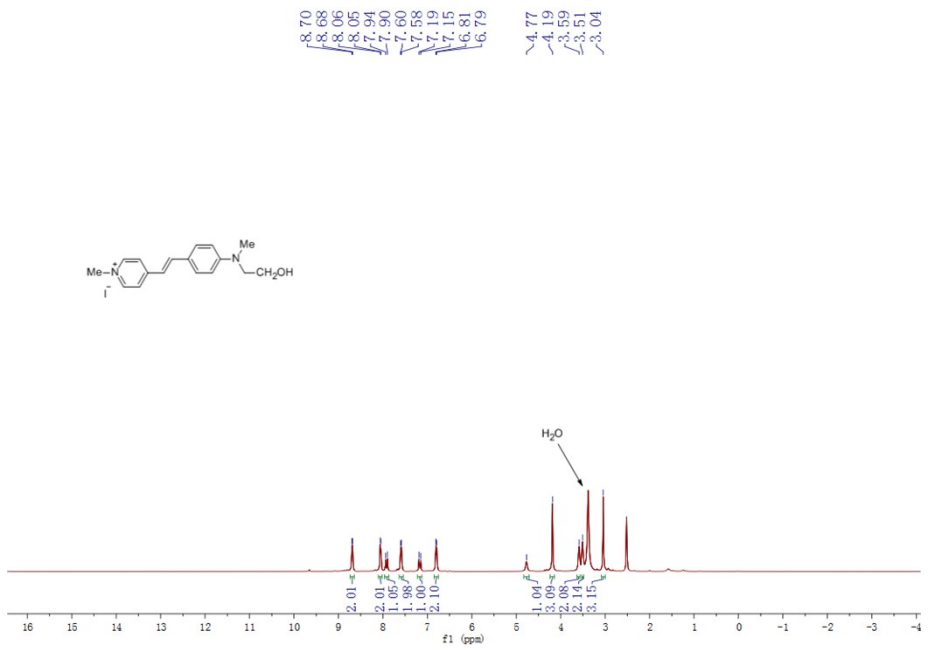
1-3	Cg(1)→Cg(1)#1	-x,1-y,1-z	3.662(3)	0	3.6461(19)	3.6462(19)
	Ring Cg(1): C(7)→C(8)→C(9)→C(10)→C(11)→C(12)→					
2	Cg(1)→Cg(1)#1	-x,y,3/2-z	3.732(4)	12	3.681(3)	3.681(3)
	Ring Cg(1): C(7)→C(8)→C(9)→C(10)→C(11)→C(12)→					

Table S5 C–H···π interaction parameters of this work

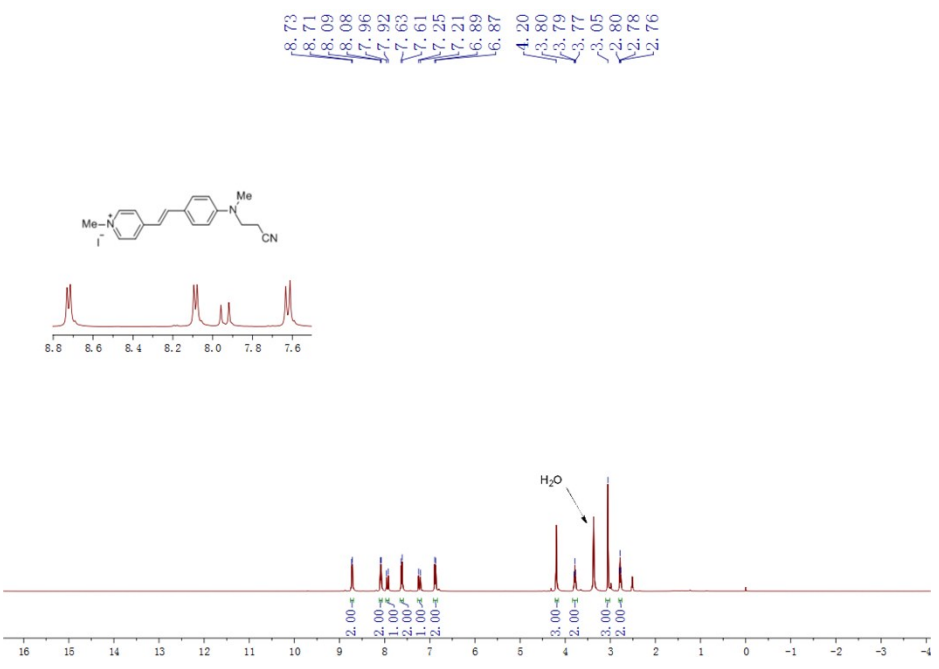
	C–H···π	C···C_g/Å	H···C_g/Å	∠(C–H···C_g)/º	Symmetry transformation
1-1	C(36)–H(36B)···C_g(1)	3.799(18)	3.804(18)	150.00	x,y,1+z
	C_g(1): C(7)→C(8)→C(9)→C(10)→C(11)→C(12)→				
1-2	C(3)–H(3)···C_g(2)	3.688(6)	2.77	170.00	-x,-y,2-z
	C(30)–H(30B)···C_g(3)	3.611(10)	2.69	161.00	1-x,1-y,1-z
	C_g(2): C(19)→C(20)→C(21)→ C(22)→C(23)→C(24)→				
	C_g(3): C(1)→C(2)→C(3)→ C(4)→C(5)→C(6)→				
1-3	C(18)–H(18)···C_g(2)	3.748(5)	2.83	169.00	-x,1-y,1-z
	C(31)–H(31B)···C_g(3)	3.582(9)	2.66	161.00	1-x,1-y,1-z
	C_g(2): C(1)→C(2)→C(3)→ C(4)→C(5)→C(6)→				
	C_g(3): C(13)→C(14)→C(15)→ C(16)→C(17)→C(18)→;				



(a)

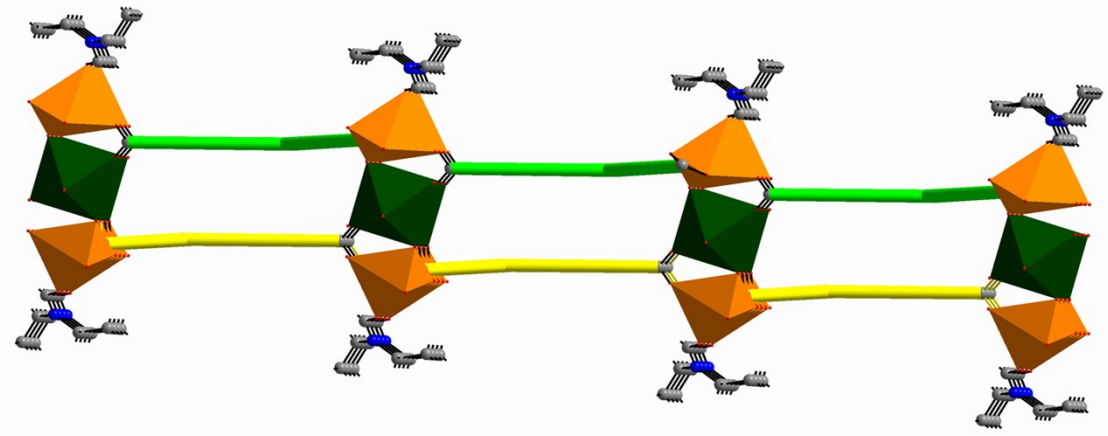


(b)

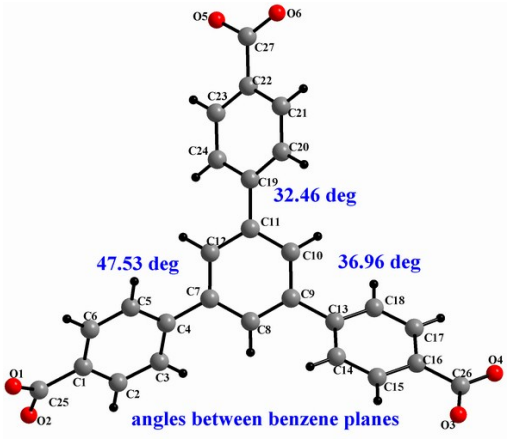


(c)

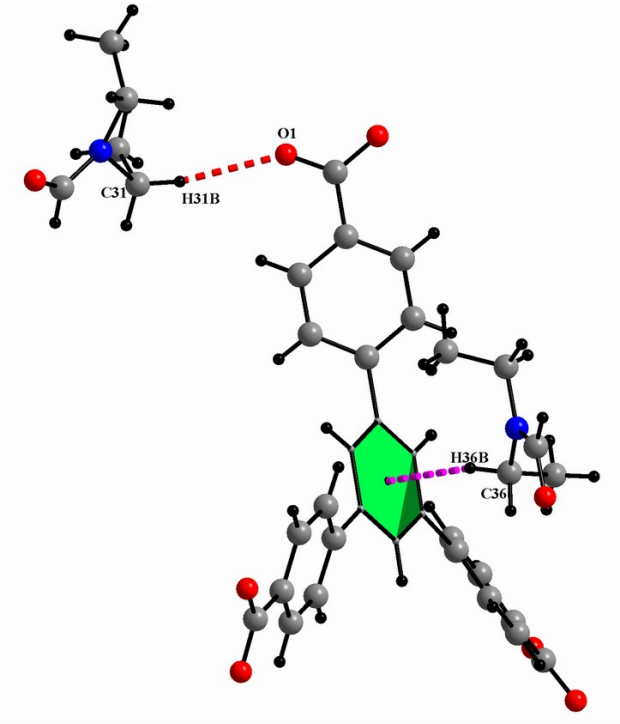
Fig. S1 ^{1}H NMR spectra of (DAST)·I (a), (HMAS)·I (b) and (CMAS)·I(c)



(a)



(b)



(c)

Fig. S2 (a) 2-D bis-layers structures showing the positions of DEF solvents; (b) angles between benzene

planes in BTB ligand of 1-1; (c) hydrogen bond and C–H···π interaction between DEF solvents and BTB liangd at adjacent bis-layer

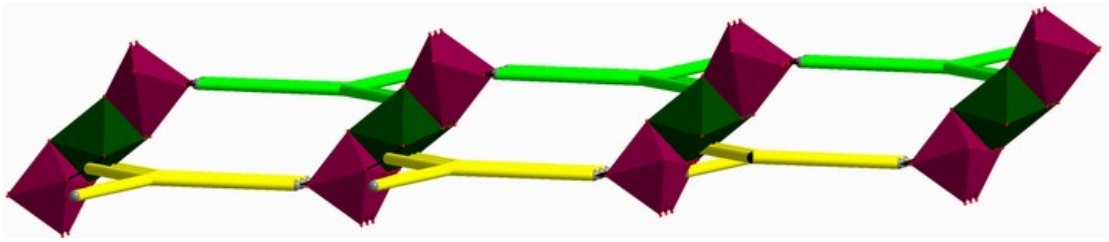
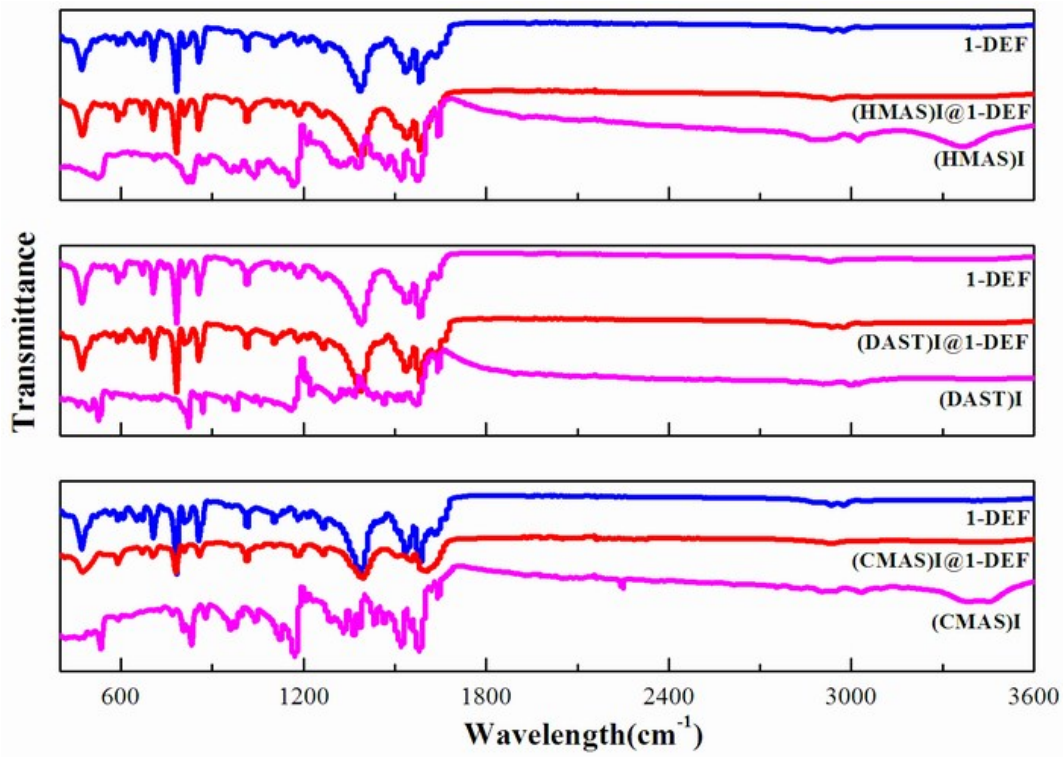
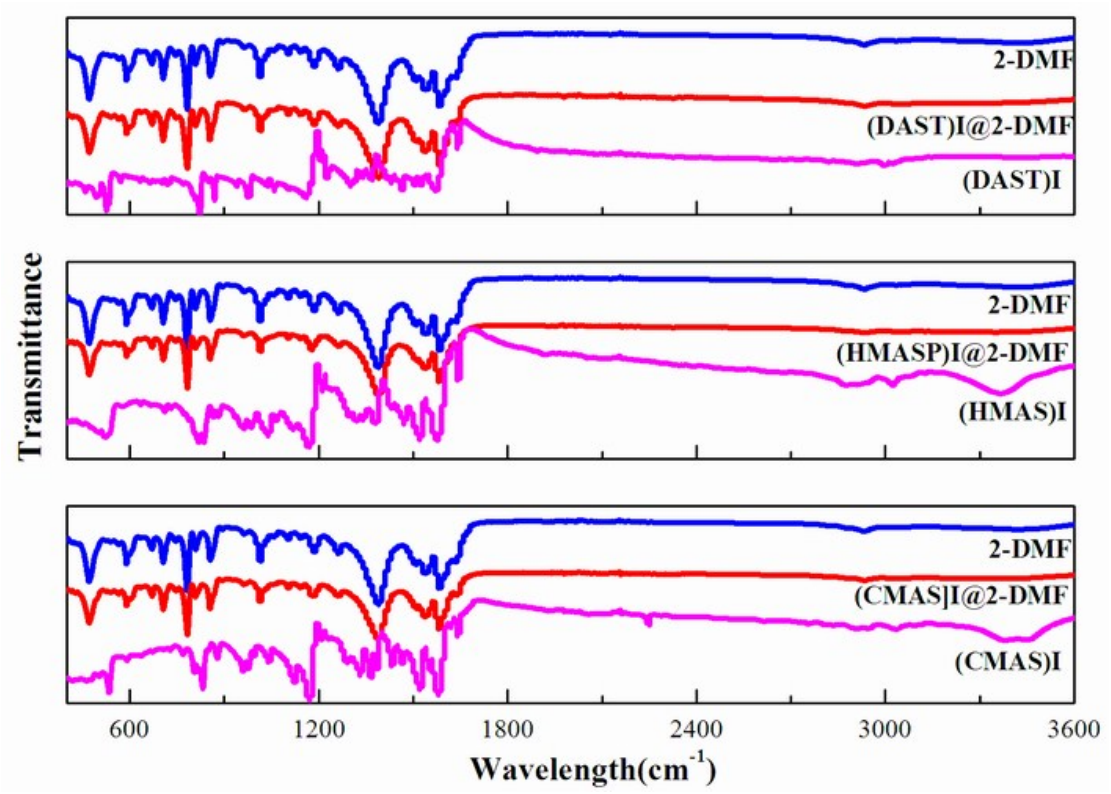


Fig. S3 2-D bis-layers showing the 1-D void 1-D channel of 2

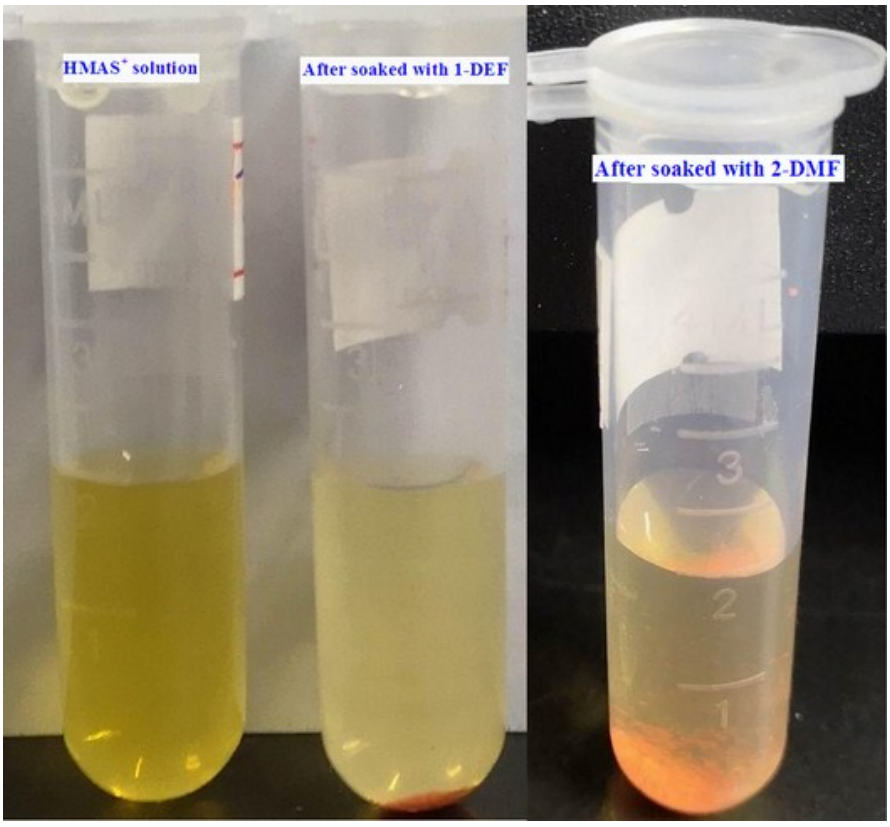


(a)

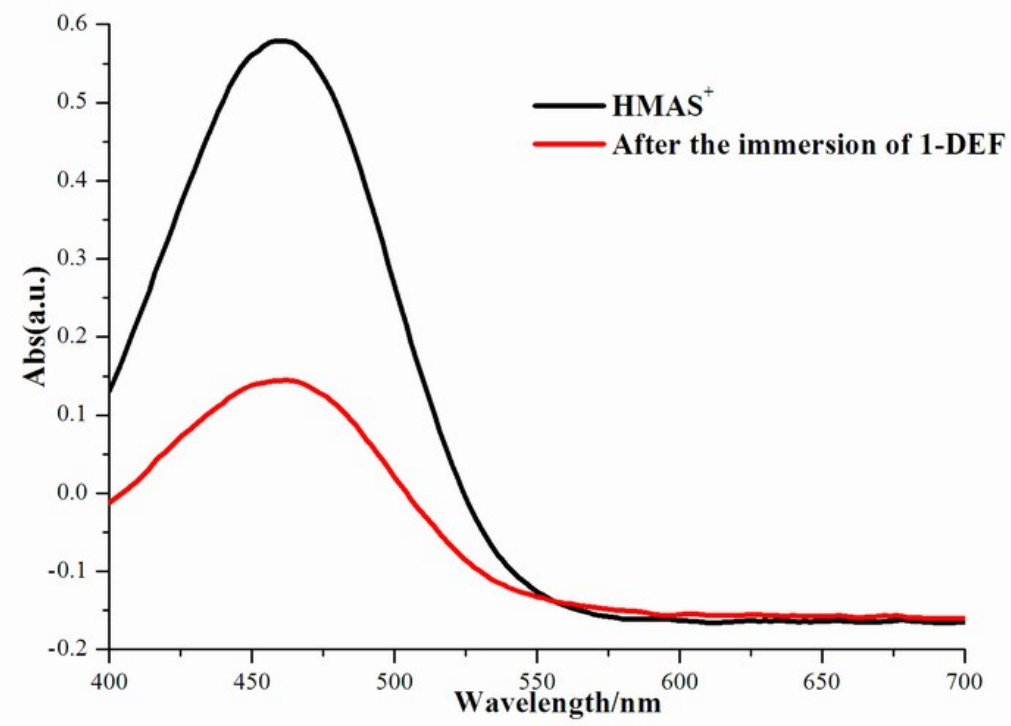


(b)

Fig. S4 IR spectra of 1-DEF, 2-DMF, pure organic dyes and dye@1-DEF (a) and dye@2-DMF composites (b) obtained from DMA solvent

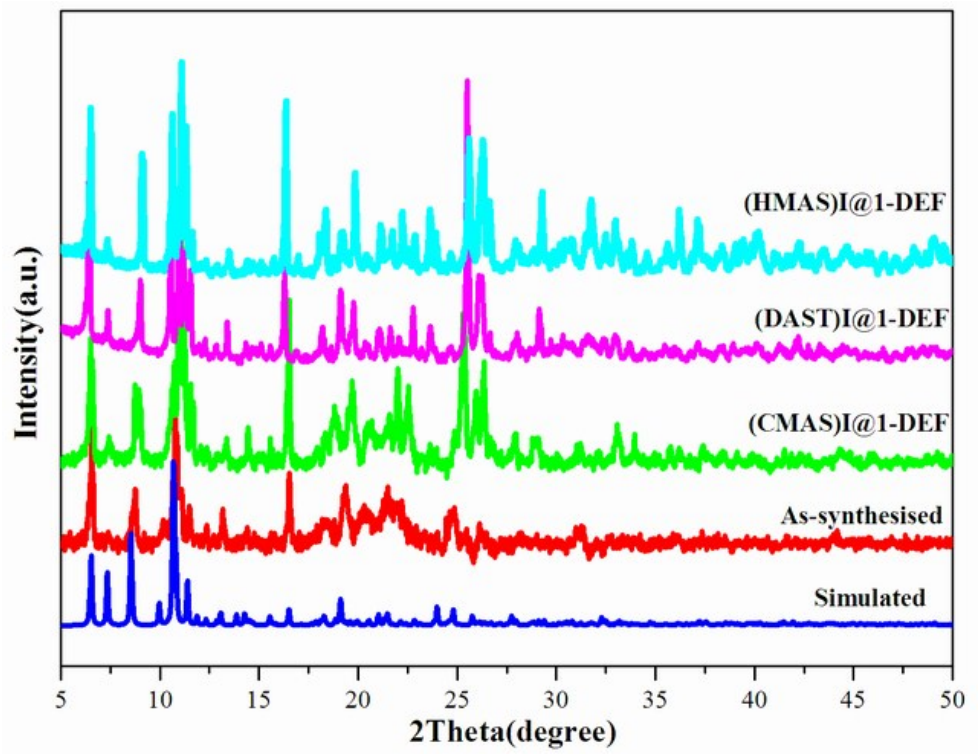


(a)

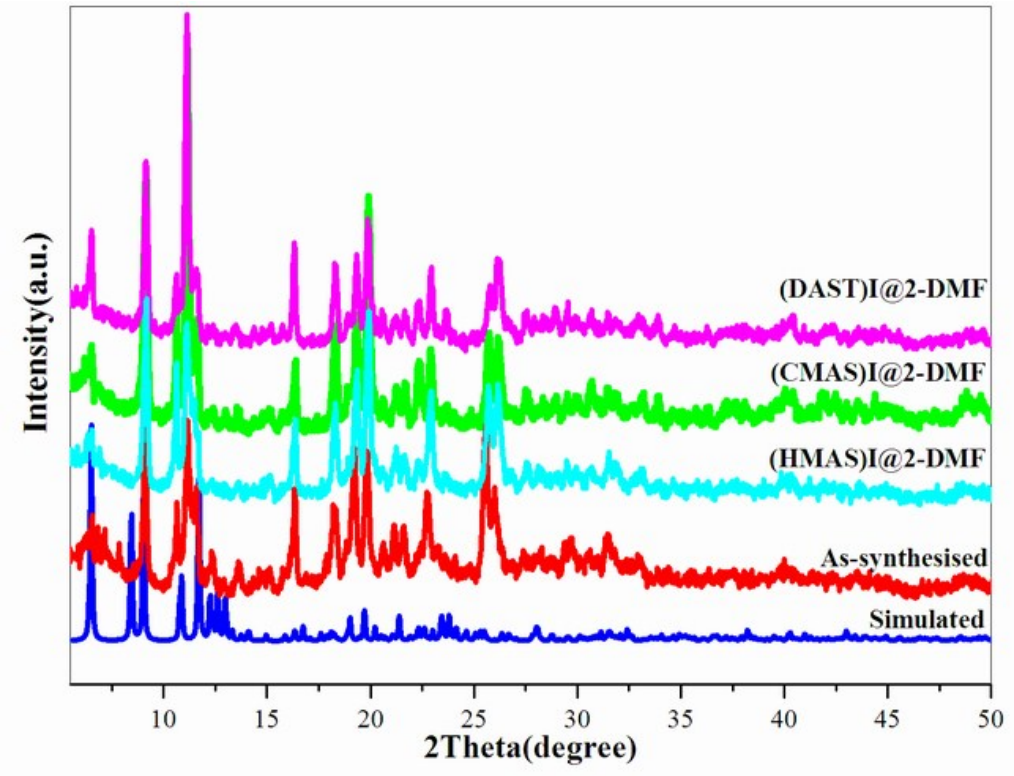


(b)

Fig. S5 (a) Photographs of $HMAS^+$ aqueous solution and its soaked with 1-DEFand 2-DMF; (b) UV-Vis spectra of $HMAS^+$ before and after the immersion of 1-DEF



(a)



(b)

Fig. S6 XRD patterns of 1-DEF (a) and 2-DMF (b) before and after the immersions of dyes

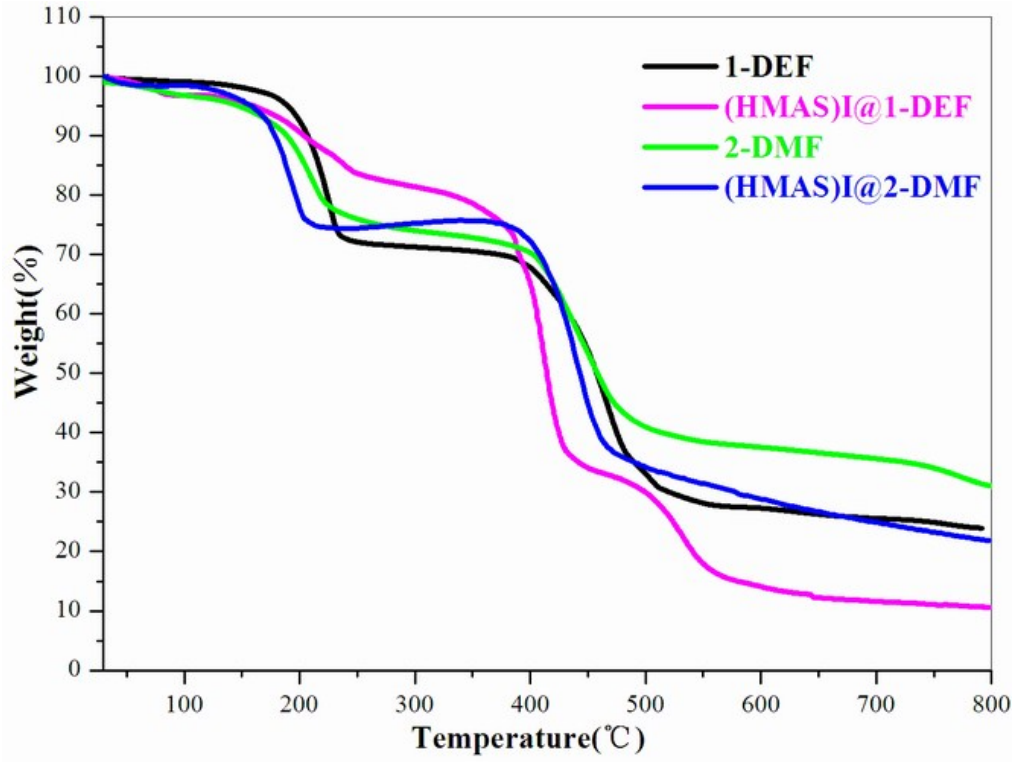
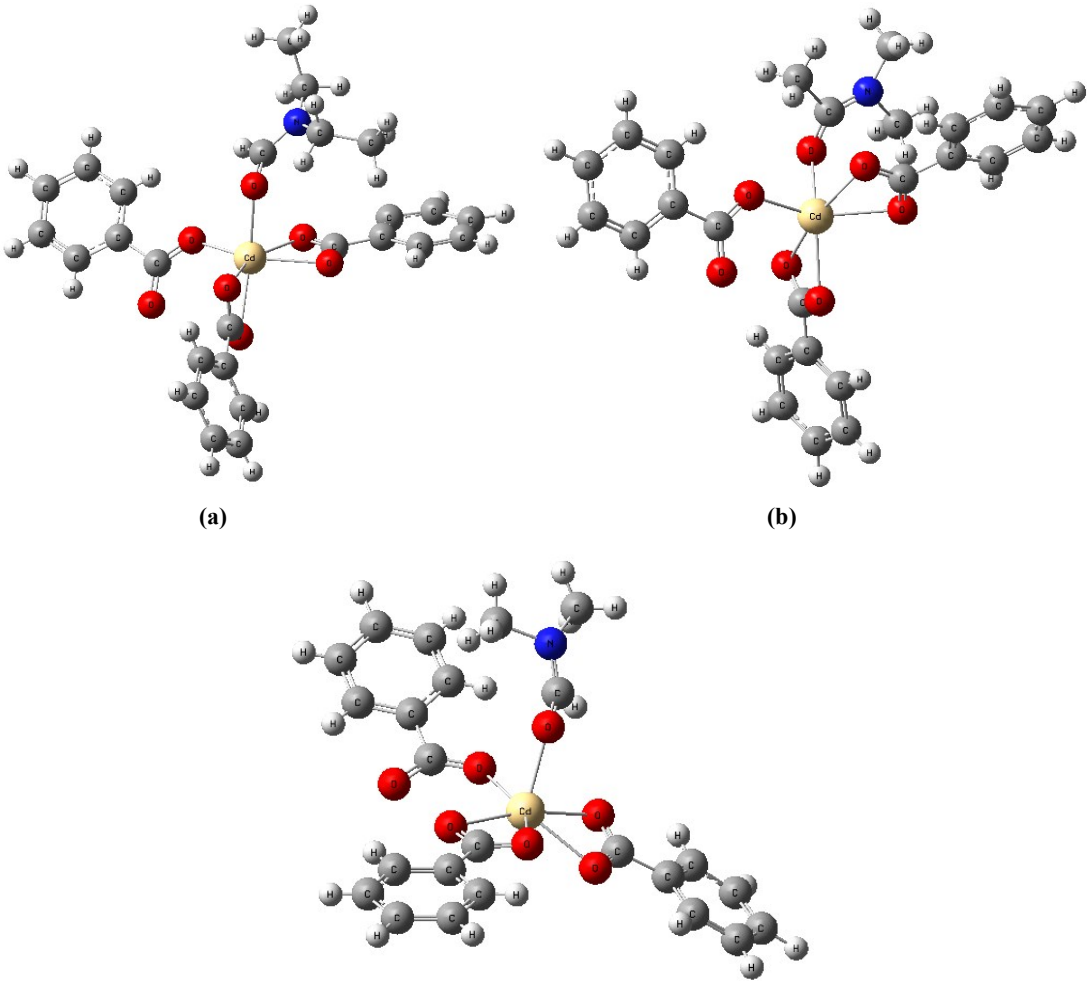


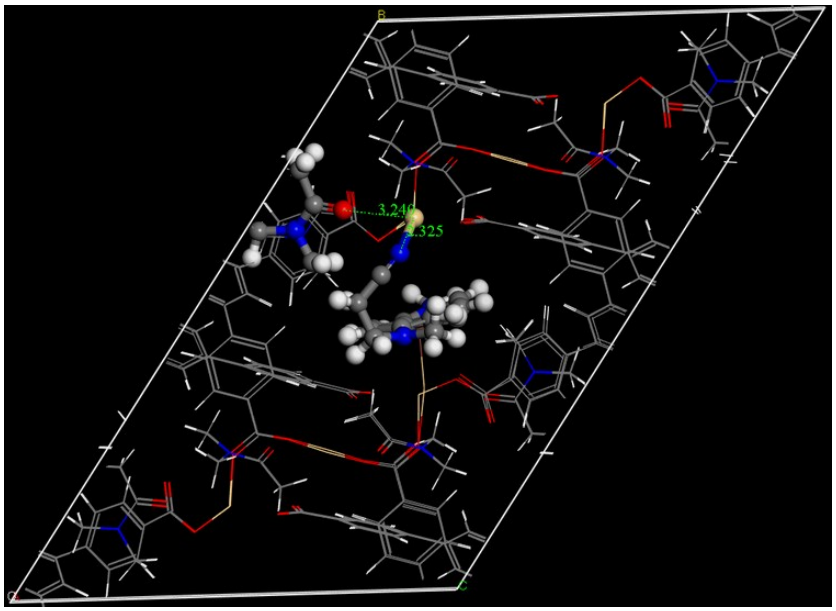
Fig. S7 TG curves of 1-DEF, 2-DMF and (HMAS)I@1-DEF and (HMAS)I@2-DMF



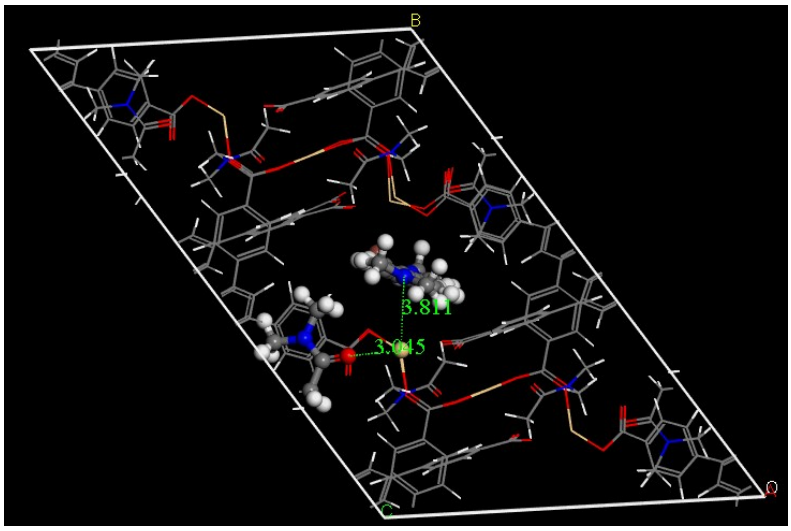
(a) **(b)**

(c)

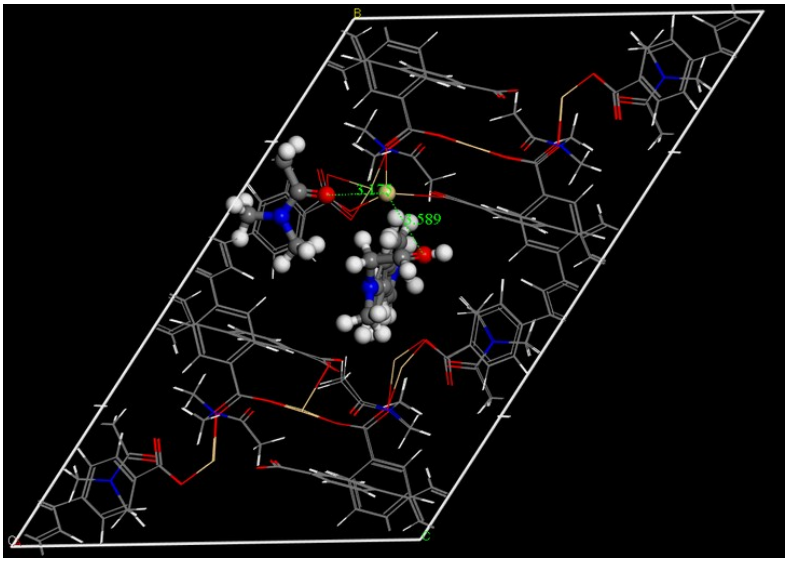
Fig. S8 Calculated models of $Cd(BA)_3DEF$ (a), $Cd(BA)_3DMA$(b) and $Cd(BA)_3DMF$ (c)



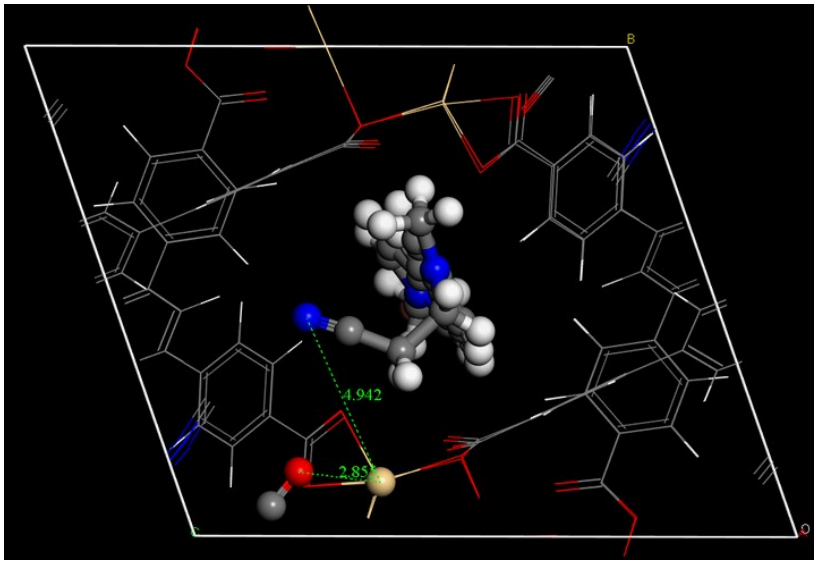
(a)



(b)

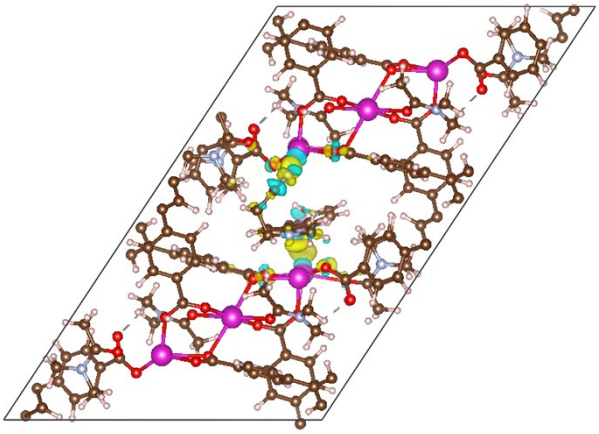


(c)

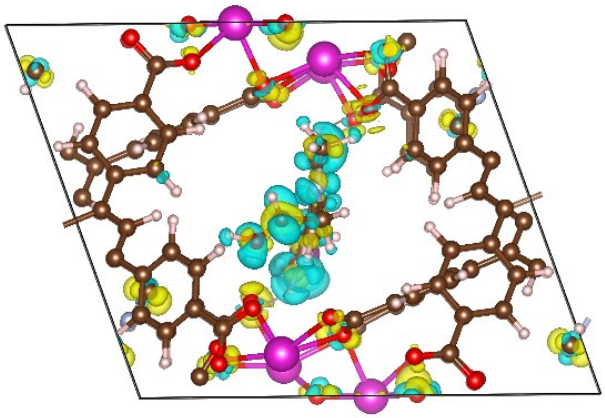


(d)

Fig. S9 The optimized structures of (CMAS)I@1-DMA (a), (DAST)I@1-DMA (b), (HMAS)I@1-DMA (c) and (CMAS)I@2-DMF (d)



(a)



(b)

Fig. S10 Difference charge density map of (CMAS)I@1-DMA (a) and (HMAS)I@1-DMA (b)

References

(1) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter Mater. Phys*. **1996**, 54, 11169−11186.

(2) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865−3868.

(3) Kresse, G.; Joubert, D. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, 59, 1758.

(4) Blochl, P. E. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, 50, 17953.

(5) 1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N.

Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A01, Gaussian, Inc., Wallingford, CT, 2009.