Supplementary Information

Synthesis, Structure Characterization and Optical Properties of a Molecular Cluster Cd_4(*p*-MBT)$_{10}$

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Solid State Structures of $[(HNEt_3)]_2[Cd_4(p\text{-}MBT)_{10}]$

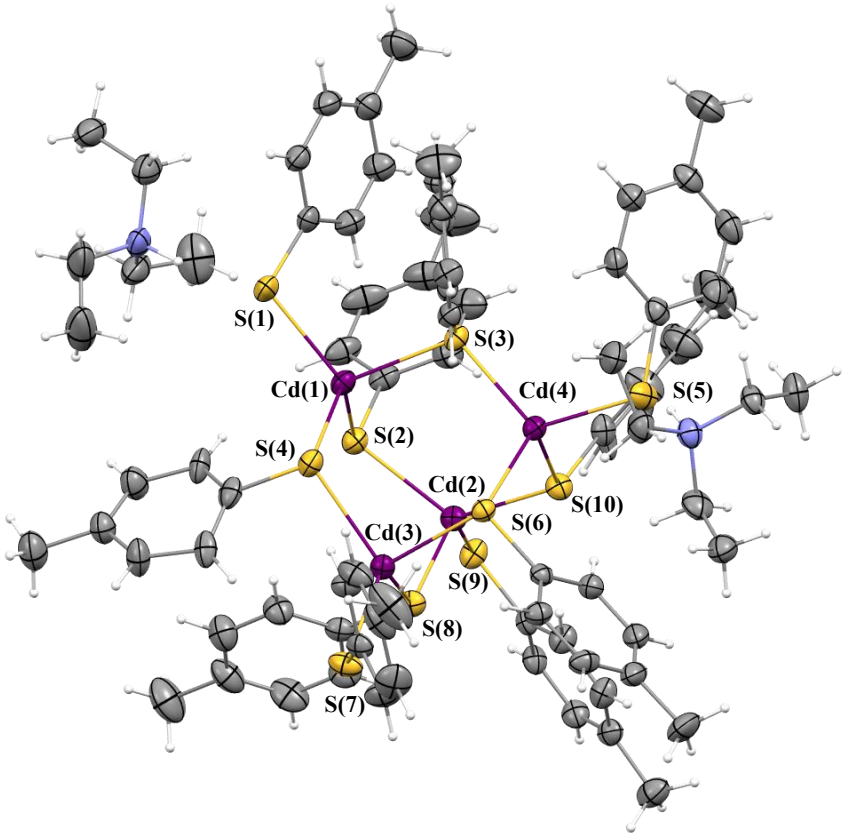


Figure S1. Solid state structure of $[(HNEt_3)]_2[Cd_4(p\text{-}MBT)_{10}]$ drawn with thermal ellipsoids at the 40% probability level. Hydrogen atoms are represented by spheres of arbitrary radius. Only cadmium and sulfur atoms are labeled.

Table S1. Selected bond distances (Å) and angles (deg.) in the structure of $[(HNEt_3)]_2[Cd_4(p\text{-}MBT)_{10}]$. Black and blue are results obtained from single crystal structure and theoretical calculation, respectively.

Bond distances		Angles		Angles	
Cd(1)–S(1)	2.498(7)/2.527	S(1)-Cd(1)-S(2)	119.42(3)/116.29	S(6)-Cd(3)-S(8)	107.25(2)/104.31
Cd(1)–S(2)*	2.564(7)/2.639	S(1)-Cd(1)-S(3)	106.37(2)/115.71	S(7)-Cd(3)-S(8)	107.59(2)/109.05
Cd(1)–S(3)*	2.545(7)/2.631	S(1)-Cd(1)-S(4)	105.74(2)/107.66	S(3)-Cd(4)-S(5)	117.71(2)/117.38
Cd(1)–S(4)*	2.561(7)/2.641	S(2)-Cd(1)-S(3)	105.20(2)/105.65	S(3)-Cd(4)-S(6)	112.28(2)/103.90
Cd(2)–S(2)*	2.568(7)/2.625	S(2)-Cd(1)-S(4)	111.03(2)/103.80	S(3)-Cd(4)-S(10)	104.51(2)/106.18
Cd(2)–S(8)*	2.547(6)/2.631	S(4)-Cd(1)-S(3)	108.65(2)/106.73	S(5)-Cd(4)-S(6)	108.30(2)/107.54
Cd(2)–S(9)**	2.459(6)/2.527	S(2)-Cd(2)-S(8)	99.28(2)/106.70	S(5)-Cd(4)-S(10)	105.11(3)/114.66
Cd(2)–S(10)*	2.556(7)/2.655	S(2)-Cd(2)-S(9)	108.16(2)/105.98	S(6)-Cd(4)-S(10)	108.27(2)/103.54
Cd(3)–S(4)*	2.584(6)/2.650	S(2)-Cd(2)-S(10)	120.64(2)/114.25		
Cd(3)–S(6)*	2.564(6)/2.635	S(8)-Cd(2)-S(9)	117.63(2)/116.29		
Cd(3)–S(7)**	2.464(7)/2.527	S(8)-Cd(2)-S(10)	98.75(2)/96.85		
Cd(3)–S(8)*	2.569(6)/2.624	S(9)-Cd(2)-S(10)	112.01(2)/116.54		
Cd(4)–S(3)*	2.519(6)/2.624	S(4)-Cd(3)-S(6)	94.61(2)/98.35		
Cd(4)–S(5)**	2.478(7)/2.526	S(4)-Cd(3)-S(7)	118.47(2)/114.94		
Cd(4)–S(6)*	2.554(6)/2.638	S(4)-Cd(3)-S(8)	113.33(2)/114.64		
Cd(4)–S(10)*	2.559(6)/2.648	S(6)-Cd(3)-S(7)	114.82(2)/114.85		

* – bridging sulfur; ** – donating sulfur

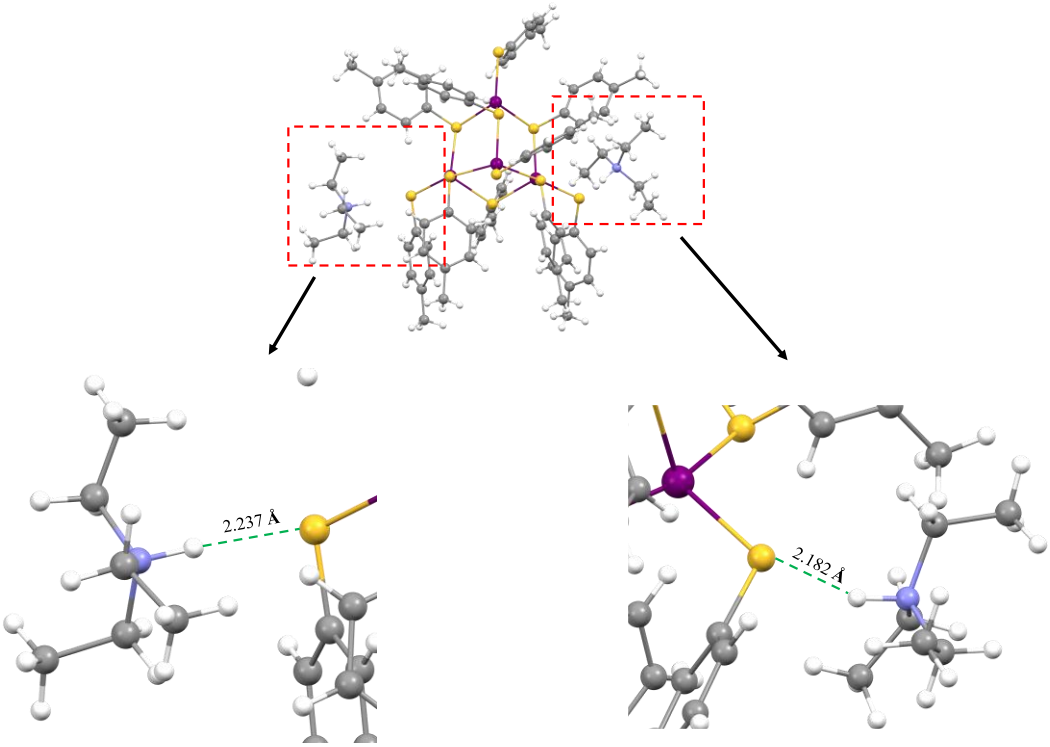


Figure S2. S···H−N hydrogen bonding in $[(HNEt_3)]_2[Cd_4(p\text{-}MBT)_{10}]$ cluster.

Table S2. N−H···S interaction comparison of the $[(HNEt_3)_2][Cd_4(p\text{-}MBT)_{10}]$ cluster with the related compound

Compound	N−H···S interaction
$[(NHEt_3)]_2[Cd_4(p\text{-}MBT)_{10}]$ (current work)	2.237 Å/2.182 Å
$(TACN)_2Fe_2S_6$ [1]	2.40 Å-2.62 Å (exp.)/2.31 Å-2.32 Å (cal.)
$[Cd(1,2\text{-}S_2\text{-}3,6\text{-}(t\text{-}BuCONH)_2C_6H_2)_2]^{2-}$ [2]	2.348 Å-2.482 Å
$[Hg^{II}(S\text{-}2\text{-}CH_3NHCOC_6H_4)_4]^{2-}$ [3]	2.319 Å

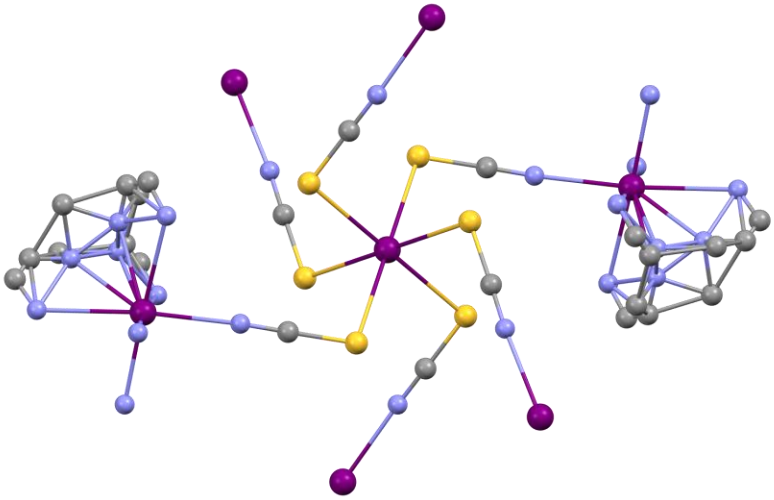


Figure S3. Total structure of $[Cd_{1.5}(bbta)_{1.5}(NCS)_3]_n$ polymer. Such a structure shows the octahedron coordination environment for Cd^{2+}. All hydrogen atoms are omitted for clarity. [4]

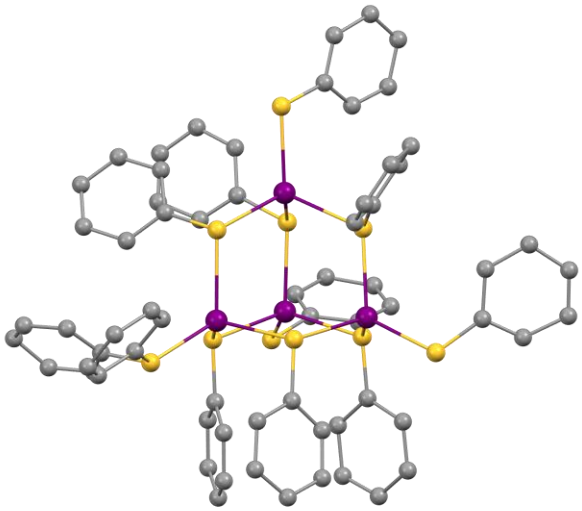


Figure S4. Total structure of $Cd_4(SPh)_{10}^{2-}$. This structure shows the Cd_4S_{10} configuration obtained from the most used thiophenol ligand. All hydrogen atoms are omitted for clarity. [5]

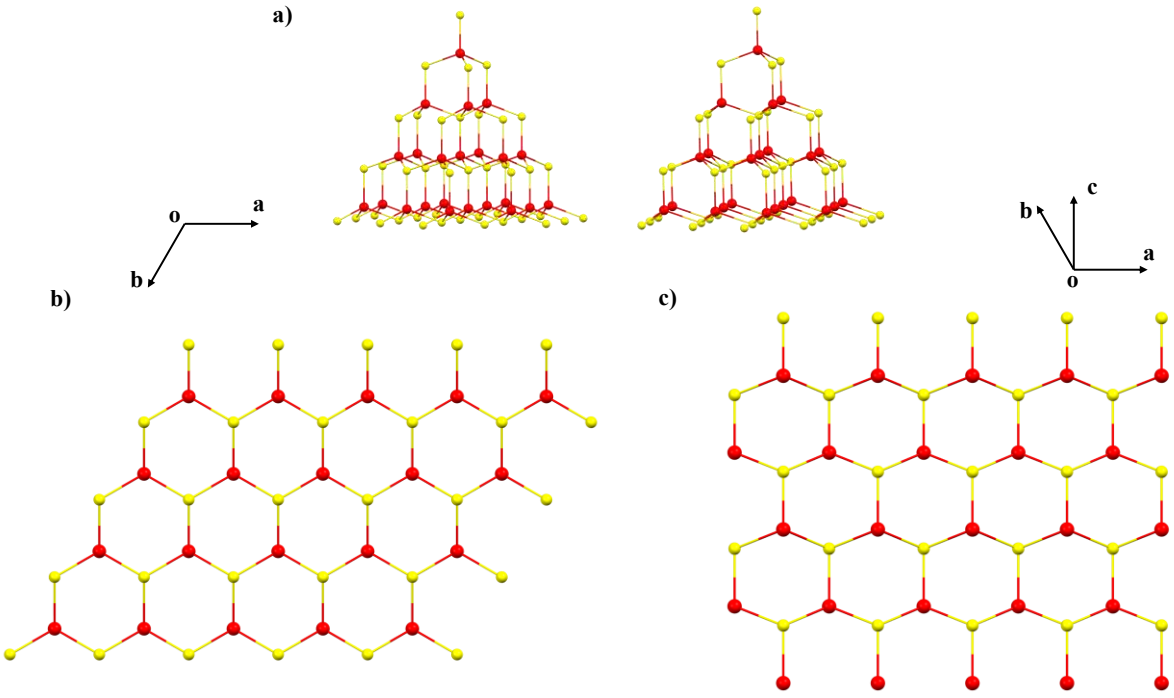


Figure S5. (a) Two views of bulk CdS wurtzite structure. (b) Viewed along c axis. Cd−S bond distance on this plane is equal. (c) Cd−S bond distance along the c axis on this plane is not equal to those in other directions. [6]

Type 1

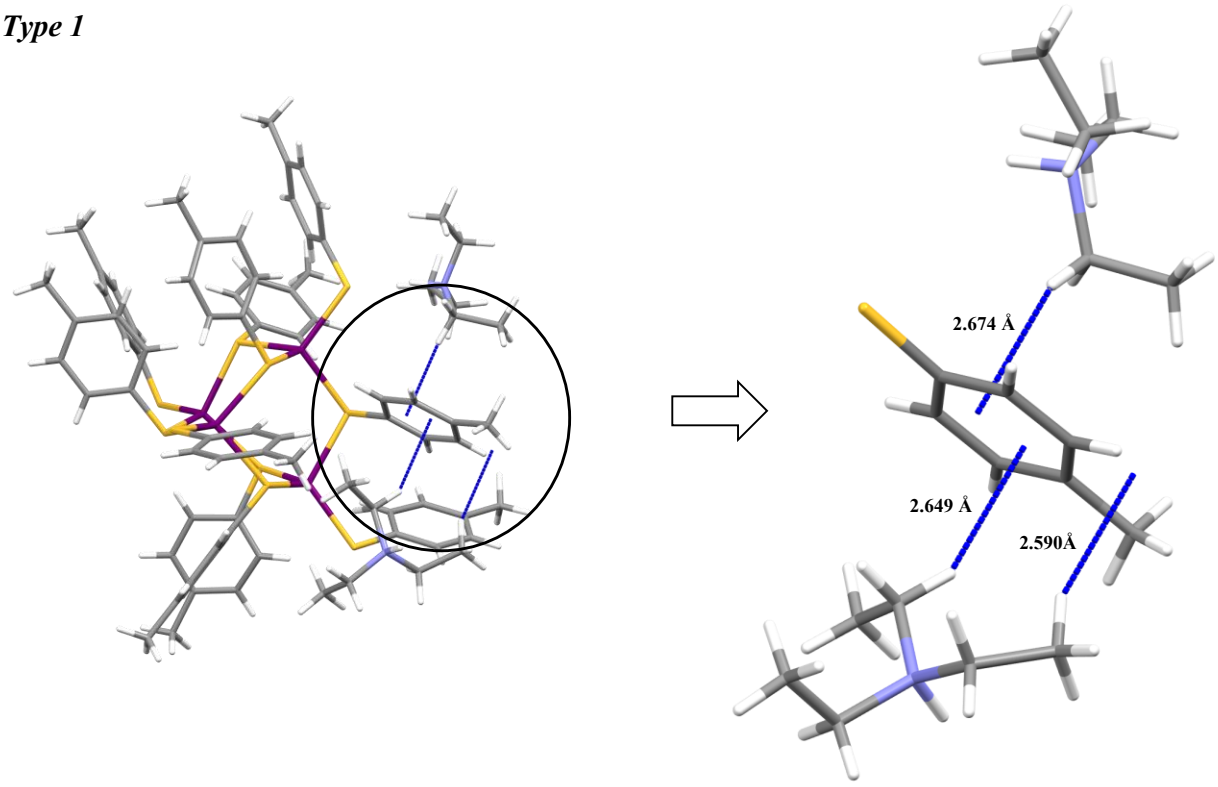


Figure S6. C−H···π interaction between *p*-MBT^{-} and $HNEt_3^{+}$: 2.590-2.674 Å.

Type 2

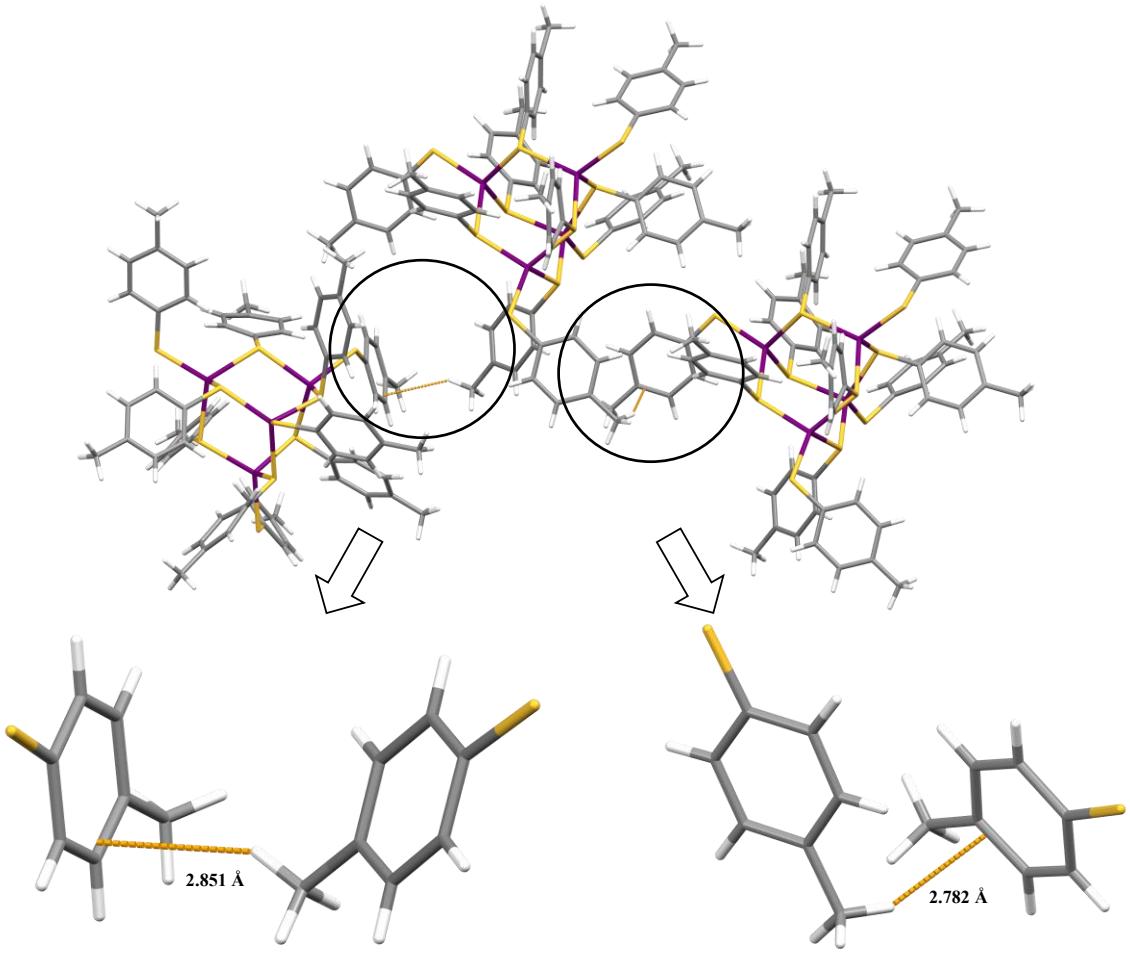
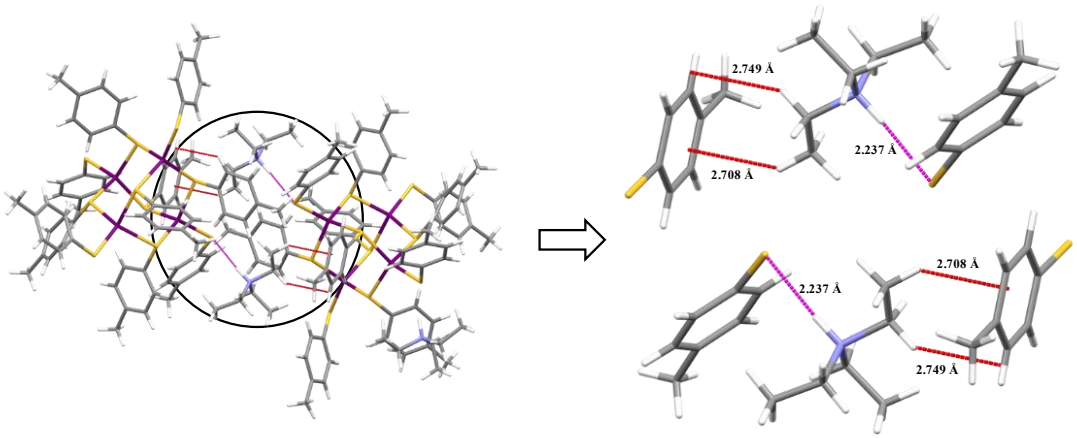


Figure S7. C−H···π interaction between the neighboring *p*-MBT⁻ ligands.

Type 3



Interaction	Distance
C-H · · ·π interaction (-----)	2.708/2.749 Å
H bonding (-----)	2.237 Å

Figure S8. C–H···π and hydrogen bonding interactions between *p*-MBT^{-} ligand and $HNEt_3^{+}$: 2.708/2.749 Å and H bonding: 2.237 Å.

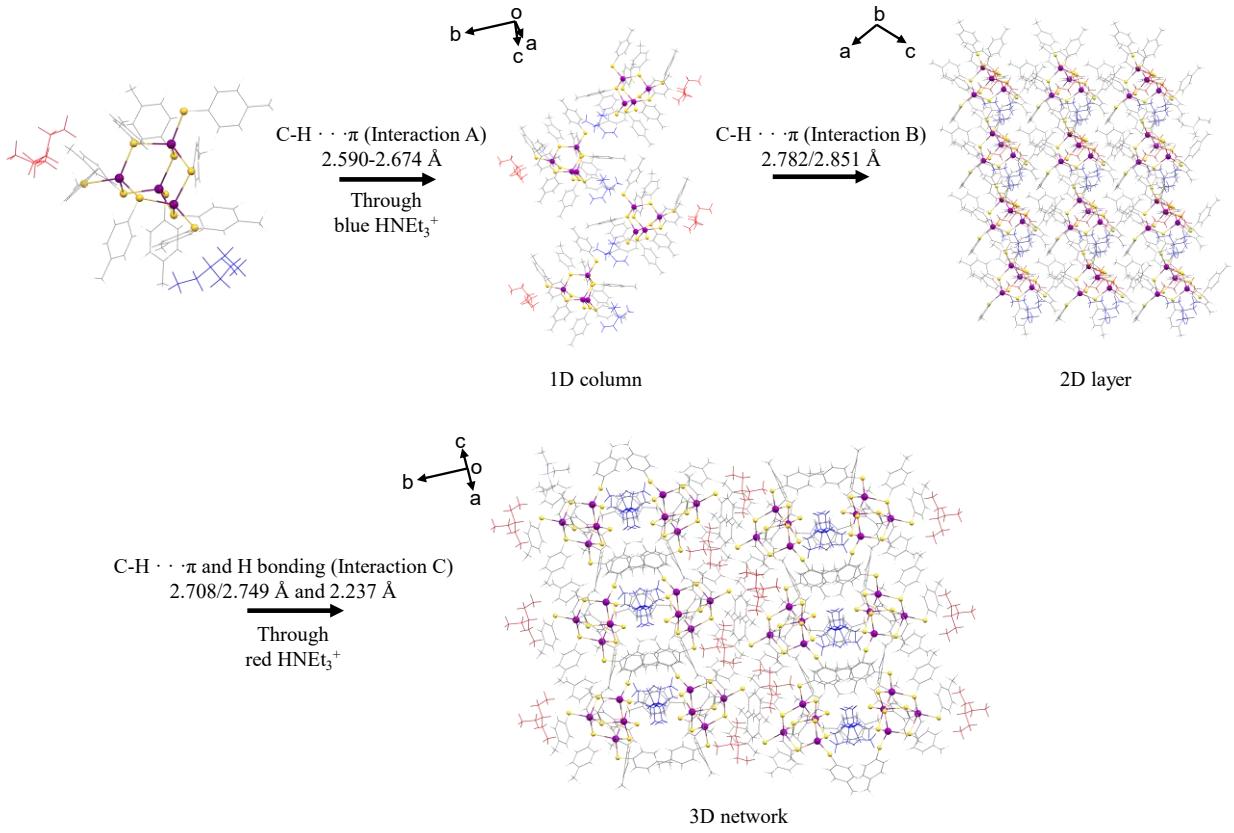


Figure S9. Single-crystal packing structure of $[(HNEt_3)_2][Cd_4(p\text{-}MBT)_{10}]$ through different interactions.

Optical Properties

Table S3. Photoluminescence excitation and photoluminescence comparison of the Cd_4(*p*-MBT)$_{10}$ cluster with the related compound

Compound	Ex. (nm)	Em. (nm)	Stokes shift (nm)
$[Cd_4(p\text{-MBT})_{10}]^{2-}$	325	360	35
$Cd_3(OH)_2Cl_2(_4\text{-PTZ})_2$ [7]	340	390	50
$[Cd_{10}S_4(SPh)_{16}]^{4-}$ [8]	350	430	80
$Cd_{32}S_{14}(SC_6H_6)_{36}\cdot DMF_4$ [9]	384	500	116
CdS NPs (~14 nm) [10]	445	536	91
CdS NPs (~21 nm) [10]	480	589	109

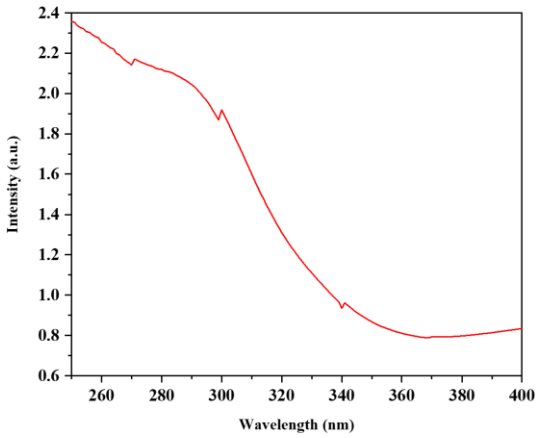


Figure S10. The UV-Vis spectrum of [(HNEt$_3$)]$_2$[Cd_4(*p*-MBT)$_{10}$].

Theoretical Calculation Details

Density functional theory (DFT) calculations were performed using the Gaussian 09 software package.[11] Due to the cost of calculation, only the Cd_4(*p*-MBT)$_{10}^{2-}$ core was evaluated. The geometry was optimized and the energy was calculated at the B3LYP/def2-TZVP level. No symmetry restrictions were used during the calculations. The calculated structures correspond to local energy minima (without imaginary frequencies). The molecular orbital (MOs) diagrams and molecular electrostatic potential (MEP) maps were generated by GaussView.

Table S4. Cartesian coordinates of the Cd_4(*p*-MBT)$_{10}^{2-}$

Tag	Symbol	X	Y	Z
1	Cd	0.234814	2.562502	-0.88821
2	Cd	-1.18716	-0.26365	2.298181
3	Cd	-0.63121	-1.70283	-1.93431
4	Cd	2.952279	-0.63854	0.512775
5	S	-2.28938	-0.52284	4.556482
6	S	0.003225	4.83152	-1.97553
7	S	1.833507	-2.31385	-1.20959
8	S	5.391082	-1.08524	1.003076
9	S	-1.35092	-3.37334	-3.68813
10	S	1.323609	-1.03547	2.545342
11	S	-2.07816	-1.65977	0.263087
12	S	-0.98634	2.235532	1.44697
13	S	2.648209	1.900377	-0.07584
14	S	-0.45193	0.810777	-2.71824
15	C	1.419486	6.902543	1.262223
16	H	1.738387	6.680182	2.275365
17	C	-4.03222	-0.76953	4.393278
18	C	-4.70177	-1.03113	3.191922
19	H	-4.14574	-1.09326	2.266002
20	C	0.566832	6.080851	-0.86144
21	C	1.572641	0.999884	4.448321
22	H	0.710353	1.470292	3.99494
23	C	2.079084	-0.18994	3.923489
24	C	-3.10264	-3.33131	-3.90697
25	C	-2.58797	3.021946	1.478795

26	C	0.994603	5.855088	0.453873
27	H	0.990439	4.851944	0.858838
28	C	3.732014	2.368489	-1.41414
29	C	3.215684	-0.74532	4.518375
30	H	3.6358	-1.65784	4.117014
31	C	-1.55612	-3.89401	1.866996
32	H	-0.90239	-3.26639	2.457545
33	C	2.883127	-2.38913	-2.64977
34	C	6.043633	-5.37633	2.574073
35	C	-2.22118	-3.37091	0.757628
36	C	1.441229	8.220378	0.808095
37	C	3.816419	-0.12955	5.607218
38	H	4.704649	-0.57864	6.039191
39	C	-4.38277	1.911384	-2.90697
40	H	-5.18204	2.117151	-2.20362
41	C	3.902064	3.726863	-1.70254
42	H	3.353349	4.46646	-1.13527
43	C	3.306887	1.051294	6.147832
44	C	4.784296	-4.97735	2.125384
45	H	3.95971	-5.6827	2.145751
46	C	-3.13696	1.541843	-2.41499
47	H	-2.98884	1.459201	-1.34688
48	C	7.06397	-4.42593	2.529611
49	H	8.057932	-4.6934	2.87597
50	C	-3.20107	-5.55085	0.38164
51	H	-3.84694	-6.18657	-0.21475
52	C	-2.30655	1.400649	-4.65933
53	H	-1.49461	1.206421	-5.34781
54	C	-2.54161	-6.08162	1.490696
55	C	-6.18534	-0.92027	5.521747
56	H	-6.74997	-0.87722	6.448717
57	C	-3.72482	-4.43748	-4.50585
58	H	-3.11701	-5.2879	-4.78956
59	C	6.839593	-3.14037	2.056503
60	H	7.652285	-2.42433	2.038968
61	C	-5.09508	-4.4627	-4.7325
62	H	-5.53599	-5.33966	-5.19711

63	C	1.936314	9.345284	1.680731
64	H	1.773178	9.128247	2.738566
65	H	1.426873	10.28397	1.449043
66	H	3.010199	9.519037	1.548766
67	C	-5.91466	-3.39498	-4.36873
68	C	5.485976	3.210559	-3.46787
69	C	-4.81371	-0.7198	5.560456
70	H	-4.32518	-0.52315	6.507096
71	C	-5.29772	-2.29513	-3.76971
72	H	-5.89603	-1.44118	-3.4689
73	C	5.315605	1.860112	-3.17118
74	H	5.861313	1.111308	-3.73482
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81	H	-6.57415	2.910953	-4.05036
82	H	-6.54185	1.504298	-5.1118
83	C	6.392048	3.658344	-4.58621
84	H	5.831532	3.823157	-5.51245
85	H	7.158936	2.910772	-4.79834
86	H	6.89423	4.597325	-4.34149
87	C	-4.61897	2.026875	-4.27607
88	C	6.292146	-6.78068	3.062576
89	H	6.347734	-7.49428	2.233342
90	H	5.492958	-7.12289	3.72517
91	H	7.233254	-6.84691	3.612878
92	C	-6.43388	5.015216	1.708133
93	H	-6.46479	5.722812	2.543133
94	H	-7.24815	4.302172	1.861316
95	H	-6.64606	5.575571	0.795661
96	C	3.9422	1.695194	7.353473
97	H	3.762283	2.77196	7.369189
98	H	5.022336	1.533781	7.367745
99	H	3.539742	1.284466	8.285781

100	C	-3.05058	-4.22011	0.019187
101	H	-3.57489	-3.8363	-0.8457
102	C	0.586038	7.410603	-1.31596
103	H	0.256554	7.620568	-2.32631
104	C	4.451802	1.440327	-2.16669
105	H	4.346139	0.381424	-1.97616
106	C	-2.07773	1.281358	-3.28582
107	C	5.573891	-2.73809	1.599826
108	C	-6.07759	-1.22672	3.164
109	H	-6.55366	-1.43018	2.210396
110	C	2.177515	1.602045	5.544741
111	H	1.760087	2.526604	5.929051
112	C	-3.92889	-2.25692	-3.5456
113	H	-3.49833	-1.37625	-3.089
114	C	-6.85205	-1.17553	4.321459
115	C	4.548937	-3.6944	1.649349
116	H	3.554624	-3.43751	1.309868
117	C	-1.72273	-5.22642	2.225121
118	H	-1.19748	-5.60258	3.096392
119	C	1.010401	8.44877	-0.50009
120	H	1.004209	9.461948	-0.8915
121	C	4.761436	4.133643	-2.71265
122	H	4.865921	5.194337	-2.91581
123	C	-5.09955	4.318774	1.621757
124	C	-2.68631	-7.5357	1.860095
125	H	-1.99684	-8.16327	1.285746
126	H	-3.69711	-7.89861	1.659902
127	H	-2.47191	-7.6995	2.917918
128	C	-8.3472	-1.36318	4.27944
129	H	-8.70069	-1.96043	5.124344
130	H	-8.6556	-1.86791	3.361865
131	H	-8.87865	-0.4057	4.317805
132	C	-3.556	1.765496	-5.14089
133	H	-3.705	1.848601	-6.21255
134	C	2.373182	-2.29995	-3.94761
135	H	1.315403	-2.14273	-4.11049
136	C	4.257297	-2.60542	-2.49734

137	H	4.685571	-2.67442	-1.50627
138	C	-4.17802	4.633114	0.625538
139	H	-4.42401	5.386199	-0.11564
140	C	5.084313	-2.7194	-3.60711
141	H	6.14561	-2.8835	-3.45169
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143	H	-5.42777	3.061239	3.336836
144	C	5.488457	-2.72122	-6.10549
145	H	5.844885	-1.73271	-6.4142
146	H	4.971689	-3.15994	-6.96194
147	H	6.368949	-3.33163	-5.89366
148	C	-3.50451	2.705127	2.488223
149	H	-3.25322	1.95657	3.228636
150	C	3.210613	-2.42281	-5.0488
151	H	2.778826	-2.35261	-6.04161
152	C	4.581497	-2.63028	-4.90505
153	C	-2.94179	4.00078	0.547906
154	H	-2.25565	4.277483	-0.24264

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