Electronic Supplementary Information

Dual-Function Fluorescent Hydrazone-Linked Covalent Organic Frameworks with Acid Vapor Sensing and Iron(III) Ion Sensing

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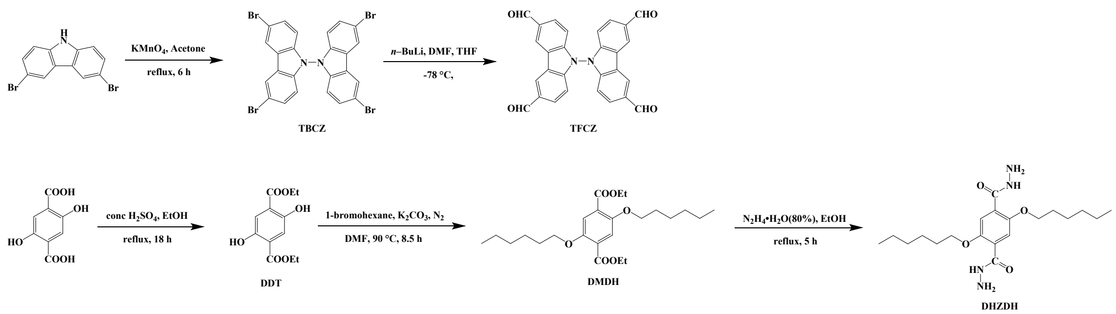
Table of Contents

Synthetic Procedures

Synthesis of monomers:



Synthesis of 3,3',6,6'-tetrabromo-9,9'-bicarbazole (TBCZ): 3, 6-dibromocarbazole (1.625 g, 5 mmol), potassium permanganate (1.975 g, 12.5 mmol) and acetone (6 mL) were added into a 250 mL two-neck flask, and the reaction mixture was reflux for 6 h. After cooled to room temperature, the reaction mixture was extracted by DCM/H_2O. The collected the organic layer was dried by anhydrous magnesium sulfate. The solvent was removed by vacuum evaporation and the crude product was purified by column chromatography to give TBCZ as a white solid with a yield of 78.7%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 1.7 Hz, 4H), 7.49 (dd, J = 8.6, 1.8 Hz, 4H), 6.76 (d, J = 8.6 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.54, 130.4, 123.95, 122.70, 115.02, 110.54.

Synthesis of 9,9'-bicarbazole]-3,3',6,6'-tetracarbaldehyde (TFCZ): TBCZ (1.296 g, 2.0 mmol) and anhydrous tetrahydrofuran (THF, 60 mL) were added to a 250 mL two necked round-bottom flask. After stirring for 15 minutes, the reaction mixture was cooled to -78 °C, then n-BuLi (2.4 M, 4.7 mL, 11.2 mmol) was added dropwise via syringe in around 5 minutes. After further stirring at -78 °C for 3 hours, a solution of dimethylformamide (3 mL) was added dropwise in 5 minutes. The reaction mixture was further stirred at -78 °C for another 2 hours, then warmed to room temperature and stirred at room temperature overnight. The reaction mixture was poured into large amount of water and extracted by DCM. Collected organic layer, dried by anhydrous magnesium sulfate. The solvent was removed by vacuum evaporation and the crude product was purified by column chromatography to give a white solid TFCZ with a yield of 30.0 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.21 (s, 4H), 8.87 (s, 4H), 8.03 (d, J =

7.0 Hz, 4H), 7.09 (d, J = 8.4 Hz, 4H). ^{13}C NMR (126 MHz, DMSO) δ 192.56, 143.51, 132.26, 129.66, 125.28, 122.57, 110.23. HRMS (ESI): m/z $[M + HCOO]^-$ calcd for $C_{29}H_{17}N_2O_6$: 489.1092; found: 489.1100.

Synthesis of diethyl 2,5-dihydroxyterephthalate (DDT): 2, 5-dihydroxy terephthalic acid (3.01 g, 15.2 mmol), ethanol (60 mL) and concentrated sulfuric acid (12 mL) were added into a 250 mL two-neck flask, and the reaction mixture was reflux for 18 h. After cooled to room temperature, the reaction mixture was poured into 200 ml ice water to precipitate white solids. The sediment was filtered and rinsed with water. The filter cake was dissolved in DCM and dried with anhydrous magnesium sulfate. The solvent was removed by vacuum evaporation and the crude product was purified by column chromatography (petroleum ether/ dichloromethane, v/v = 2:1) to give DDT as a green solid with a yield of 95.53%. ^1H NMR (500 MHz, $CDCl_3$) δ 10.15 (s, 2H), 7.50 (s, 2H), 4.45 (s, 4H), 1.43 (s, 6H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 169.07, 152.93, 118.49, 117.69, 62.01, 14.05.

Synthesis of diethyl 2-(hexyloxy)-5-((hexyloxy)methyl)terephthalate (DMDH): Diethyl 2,5-dihydroxyterephthalate DDT (1 g, 3.9 mmol), K_2CO_3 (2.49 g, 18.05 mmol) and 1-bromohexane (1.03 g, 9.45 mmol) were suspended in dimethylformamide (20 ml). The resulting mixture was refluxed at 90 °C under N_2 atmosphere for 8.5 h. After cooled to room temperature, the reaction mixture was poured into large amount of water and extracted by dichloromethane. Collected organic layer, dried by anhydrous magnesium sulfate. The solvent was removed by vacuum evaporation and the crude product was purified by column chromatography (petroleum ether/ dichloromethane, v/v = 2:1) to give DMDH as a colorless oil with a yield of 85.6%.^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (s, 2H), 4.34 (q, J = 7.1 Hz, 4H), 3.97 (t, J = 6.5 Hz, 4H), 1.80 – 1.74 (m, 4H), 1.48 – 1.42 (m, 4H), 1.36 (t, J = 7.1 Hz, 6H), 1.33 – 1.29 (m, 8H), 0.90 – 0.86 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.14, 151.74, 124.79, 116.82 – 116.39, 69.99, 61.27, 31.51, 29.23, 25.67, 22.56, 14.22, 13.99.

Synthesis of 2,5-bis(hexyloxy)terephthalohydrazide (DHZDH): Diethyl 2,5-bis(hexyloxy)terephthalate DMDH (1.125 g, 3.625 mmol), hydrazine hydrate (2.12 ml, 43.5 mmol) and ethanol (15 ml) were added in a flask and reflux at 84 °C under N_2 atmosphere for 5 h. The mixture was cooled to 0 °C, and white solid precipitates out. The precipitates was filtered and washed with ethanol, and then dried under vacuum to afford a white solid with a yield of 74.55%. The product does not require further purification. ^{1}H NMR (500 MHz, DMSO) *δ* 9.21 (s, 2H), 7.39 (s, 2H), 4.57 (d, *J* = 4.2 Hz, 4H), 4.06 (t, *J* = 6.6 Hz, 4H), 1.80 – 1.70 (m, 4H), 1.45 – 1.28 (m, 12H), 0.92 – 0.80 (m, 6H). ^{13}C NMR (500 MHz, $CDCl_3$) *δ* 165.39, 150.84, 123.09, 115.81, 69.95, 31.39, 29.06, 25.68, 22.52, 13.96. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{34}N_4O_4$: 395.2653; found: 395.2672.

N_2 adsorption–desorption isotherms curves

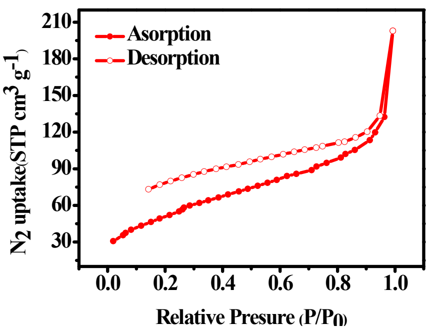


Fig. S1 N_2 adsorption–desorption isotherms curves for CZ-DHZ-COF.

SEM images

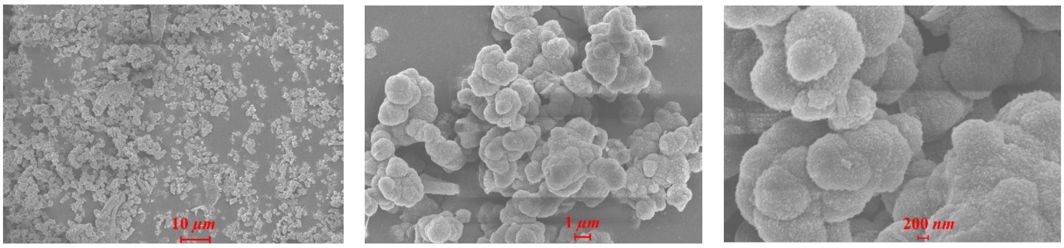


Fig. S2 SEM images of CZ-DHZ-COF.

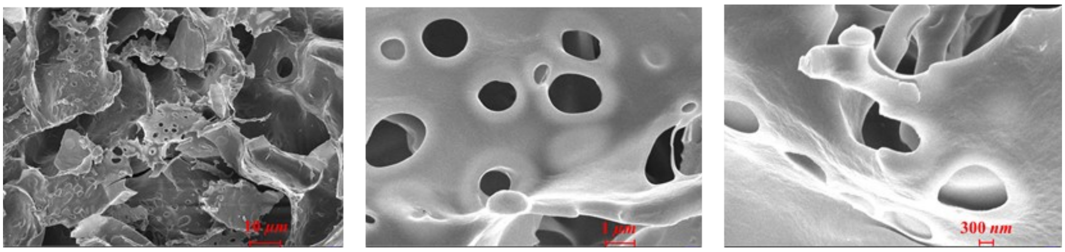


Fig. S3 SEM images of Chitosan aerogel.

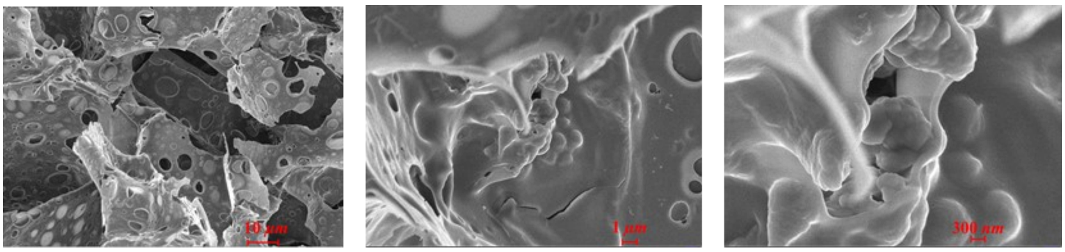


Fig. S4 SEM images of CZ-DHZ-COF&Chitosan aerogel.

Fluorescence emission spectra

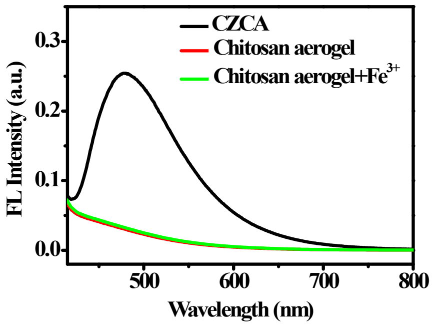


Fig. S5 Fluorescence emission spectra of CZCA, Chitosan aerogel and that of treated with Fe^{3+} (10^{-4} M).

Atomic Coordinates

Table S1 Atomistic coordinates for the AA-stacking mode of CZ-DHZ-COF

CZ-DHZ-COF(AA Spacking): Space group symmetry P1 **a = b = 23.17 Å, c = 4.89 Å** **α = β = γ = 90°**							
Atom	X	Y	Z	Atom	X	Y	Z
N1	-0.5226	-0.1707	-0.938	H82	-0.2499	-0.5395	-0.0478
O2	-0.4789	-0.1407	-0.5536	H83	-0.483	-0.8521	-0.9653
C3	-0.5049	-0.1281	-0.7618	H84	-0.628	-0.9733	-0.9498
O4	-0.6157	-0.0865	-0.9734	H85	-0.1475	-0.4396	-0.3236
C5	-0.572	-0.0468	-0.9061	H86	-0.0873	-0.563	-0.3132
C6	-0.5176	-0.0662	-0.8149	C87	-0.4424	-0.905	-0.4323
C7	-0.4752	-0.0252	-0.7502	C101	-0.3872	-0.8712	-0.3698
O8	-0.8746	-0.4958	-0.2681	C102	-0.3704	-0.8285	-0.5966
N9	-0.8646	-0.5562	0.0887	C103	-0.3276	-0.7821	-0.4955
C10	-0.8971	-0.5221	-0.0803	C104	-0.3552	-0.7225	-0.4473
O11	-0.9797	-0.5905	-0.3979	C105	-0.4049	-0.7239	-0.2433
C12	-0.9598	-0.5175	-0.0422	H116	-0.3942	-0.8474	-0.1769
C13	-0.9811	-0.4768	0.1436	H117	-0.4096	-0.8079	-0.6836
C14	-0.9986	-0.5495	-0.2061	H118	-0.2935	-0.7765	-0.6532
C15	-0.7097	-0.5218	-0.0146	H119	-0.3708	-0.7041	-0.6427
C16	-0.6865	-0.572	-0.1388	H120	-0.3909	-0.7452	-0.0526
C17	-0.6308	-0.5685	-0.2464	H131	-0.4463	-0.9404	-0.2802
C18	-0.5987	-0.5183	-0.2314	H132	-0.4801	-0.8759	-0.4105
C19	-0.6196	-0.4696	-0.0988	H151	-0.351	-0.9019	-0.3364
C20	-0.6755	-0.4715	0.0094	H152	-0.3494	-0.8536	-0.7624
C21	-0.5974	-0.6079	-0.3885	H153	-0.3052	-0.7964	-0.3061
C22	-0.5471	-0.5793	-0.4563	H154	-0.3214	-0.6929	-0.3679
N23	-0.5474	-0.5246	-0.3593	H155	-0.4427	-0.7473	-0.3279
C24	-0.6061	-0.6659	-0.4561	H156	-0.4184	-0.6791	-0.1963
C25	-0.562	-0.6948	-0.6024	C88	-0.6385	-0.0804	-1.2447
C26	-0.5116	-0.664	-0.6806	C106	-0.7002	-0.1047	-1.2593
C27	-0.5038	-0.6062	-0.6064	C107	-0.7042	-0.162	-1.4158
N28	-0.5019	-0.4843	-0.3692	C108	-0.68	-0.213	-1.2524
C29	-0.4469	-0.4926	-0.2856	C109	-0.6872	-0.2694	-1.4126
C30	-0.4134	-0.4445	-0.3374	C110	-0.6637	-0.3207	-1.253
C31	-0.4497	-0.4042	-0.4566	H121	-0.7187	-0.1095	-1.0511
C32	-0.5033	-0.4301	-0.473	H122	-0.6813	-0.1582	-1.6146
C33	-0.4402	-0.3479	-0.5497	H123	-0.7033	-0.2164	-1.0546

C34	-0.4874	-0.3176	-0.6639	H124	-0.6639	-0.2662	-1.6104
C35	-0.542	-0.3451	-0.6832	H125	-0.671	-0.3609	-1.3716
C36	-0.5502	-0.4015	-0.5875	H133	-0.6094	-0.1027	-1.3907
C37	-0.4237	-0.5416	-0.1631	H134	-0.6401	-0.0344	-1.3107
C38	-0.3647	-0.542	-0.1022	H157	-0.7278	-0.0728	-1.3684
C39	-0.3295	-0.4937	-0.1635	H158	-0.7505	-0.1704	-1.4609
C40	-0.3545	-0.4435	-0.2792	H159	-0.6335	-0.2057	-1.21
C41	-0.7707	-0.5183	0.0666	H160	-0.7337	-0.2769	-1.456
C42	-0.566	-0.7574	-0.657	H161	-0.6859	-0.3247	-1.0529
C43	-0.4805	-0.2569	-0.7518	H162	-0.6166	-0.3154	-1.219
C44	-0.2668	-0.4988	-0.1204	C89	-0.9451	-0.6364	-0.2901
N45	-0.8049	-0.5625	0.0504	C96	-0.9645	-0.6942	-0.4099
N46	-0.5232	-0.2297	-0.8674	C97	-0.927	-0.7446	-0.3044
N47	-0.5219	-0.8409	-0.8748	C98	-0.8843	-0.7686	-0.5168
O48	-0.6102	-0.8724	-0.7574	C99	-0.8381	-0.7255	-0.6137
C49	-0.5604	-0.8841	-0.8148	C100	-0.795	-0.7094	-0.3902
O50	-0.4408	-0.9284	-0.7014	H111	-1.0101	-0.7015	-0.347
N51	-0.5292	-0.7814	-0.8225	H112	-0.9562	-0.7805	-0.2449
C52	-0.4867	-0.9659	-0.7591	H113	-0.9092	-0.784	-0.6967
C53	-0.5428	-0.9462	-0.8281	H114	-0.8584	-0.686	-0.6979
C54	-0.5846	-0.9874	-0.9007	H115	-0.8162	-0.6845	-0.2249
N55	-0.1714	-0.4622	-0.1784	H135	-0.9482	-0.639	-0.0634
O56	-0.1668	-0.5095	0.2241	H136	-0.8995	-0.6285	-0.3461
C57	-0.142	-0.491	0.0229	H145	-0.964	-0.6921	-0.6367
O58	-0.0585	-0.4221	0.3431	H146	-0.9034	-0.7323	-0.1162
N59	-0.2319	-0.4578	-0.194	H147	-0.8626	-0.8071	-0.4285
C60	-0.0403	-0.4656	0.1623	H148	-0.8136	-0.7461	-0.7832
C61	-0.0791	-0.498	0.0002	H149	-0.7605	-0.682	-0.4797
C62	-0.0577	-0.5387	-0.1859	H150	-0.7748	-0.7487	-0.3026
H63	-0.5437	-0.1591	-1.1174	C90	-0.0943	-0.378	0.2267
H64	-0.4326	-0.0393	-0.6872	C91	-0.0804	-0.3199	0.358
H65	-0.8852	-0.5827	0.2308	C92	-0.119	-0.2709	0.2497
H66	-0.9514	-0.4518	0.2672	C93	-0.1833	-0.2781	0.3265
H67	-0.7116	-0.6111	-0.1607	C94	-0.2203	-0.2966	0.0813
H68	-0.5944	-0.4305	-0.0863	C95	-0.2822	-0.31	0.1678
H69	-0.6928	-0.4331	0.105	H137	-0.14	-0.3888	0.2688
H70	-0.645	-0.6882	-0.393	H138	-0.0879	-0.3745	0.0019
H71	-0.4772	-0.6853	-0.7898	H139	-0.0853	-0.3232	0.5832
H72	-0.4645	-0.5838	-0.6585	H140	-0.1031	-0.23	0.3414
H73	-0.3981	-0.3282	-0.5312	H141	-0.1883	-0.3099	0.4949
H74	-0.5788	-0.3225	-0.7671	H142	-0.2211	-0.2611	-0.0715
H75	-0.5921	-0.4216	-0.5991	H143	-0.3018	-0.2721	0.2706
H76	-0.4499	-0.579	-0.1215	H144	-0.3084	-0.3209	-0.015

H77	-0.346	-0.5805	-0.0131	H126	-0.0346	-0.309	0.3143
H78	-0.3288	-0.4059	-0.3286	H127	-0.1133	-0.2665	0.0249
H79	-0.7883	-0.4766	0.1248	H128	-0.2	-0.2362	0.4036
H80	-0.5965	-0.7827	-0.5403	H129	-0.2017	-0.3355	-0.0174
H81	-0.4398	-0.2352	-0.7168	H130	-0.2827	-0.3475	0.3093