A Multiresponsive Metal–Organic Framework: Direct Chemiluminescence, Photoluminescence, and Dual Tunable Sensing Applications

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By incorporating an anthracene moiety into a framework, a multiresponsive luminescent metal–organic framework (1) has been synthesized, which exhibits both direct chemiluminescence (CL) and dual tunable photoluminescence. By utilizing the CL, 1 has been explored as a selective visual sensor for hydrogen peroxide. Moreover, 1 also exhibits tunable fluorescence response toward different analytes. For electron-rich aromatics, "turn-on" and "turn-off" responses can be simply switched by varying the excitation wavelength. For nitroaromatics, 1 exhibits novel linear quantitative quenching response. Density functional theory (DFT) calculations and experiments have been carried out to study the unique fluorescence response. The multiple luminescence properties and dual tunable sensing response indicate that incorporating anthracene moieties into frameworks should be a promising strategy to develop unprecedented luminescent materials with remarkable sensing properties.

1. Introduction

Microporous luminescent materials have gained considerable interest in fundamental and practical research due to their potential applications in optical devices,[1] photocatalysis,[2] and sensing.[3] The signal transduction of the currently reported stimuli-responsive luminescent materials was mostly achieved based on the change of fluorescence produced by light irradiation (photoluminescence, PL), either in a way of fluorescence quenching or enhancement, which cannot satisfy the sophisticated requirements of sensing in nature. Under such circumstances, exploring other signal transduction will help to overcome the existing issues and may expand the research in sensing science. Metal–organic frameworks (MOFs), which are built by rationally connecting the functional organic molecules with inorganic nodes, have shown promising applications and potentials in many fields, such as gas storage, electronics, catalysis, and sensing.[4–7] The rational designed linkers and crystal engineering theory make MOFs excellent candidates for the fabrication of multiresponsive luminescent materials with remarkable sensing abilities.

Generally, π-conjugated molecules exhibit promising potentials in constructing functional materials and luminescent MOFs.[8] The anthracene derivatives are an important class of π-conjugated compounds in constructing functional materials with unique properties, among which the carboxylate functionalized anthracene derivatives are excellent linkers in constructing luminescent MOFs.[9] Most of the reported sensing MOFs acted as "turn-off" fluorescence sensors and a few of them acted as "turn-on" fluorescence sensors. To the best of our knowledge, MOFs with dual sensing behavior which could easily switch their sensing behaviors from "turn-off" to "turn-on" toward a specific analyte reversibly have not been reported yet.[10] Currently, the research in CL of MOFs is still in its infancy, and no direct chemiluminescent MOFs have been reported.[11] During our research we found that linear polycyclic aromatic hydrocarbons are excellent CL agent, which inspired us to study the possibility of constructing MOFs exhibiting both direct CL and PL based on anthracene derivatives. Hence, we report the first example of MOFs exhibiting both direct chemiluminescent and photoluminescent behaviors, as well as its applications as a potential visual sensor for hydrogen peroxide and a dual fluorescence sensor for electron-rich/deficient aromatics.

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2. Results and Discussion

2.1. Synthesis and Structures

The solvothermal reaction of (2*E*,2′*E*)-3,3′-(anthracene-9,10-diyl) diacrylic acid (H_2**L**) with $Cd(NO_3)_2 \cdot 4H_2O$ in a mixed solvent of *N*,*N*-dimethylformamide (DMF) and H_2O yielded yellow sheet-like crystals of $[Cd_2\mathbf{L}_2(DMF)_2] \cdot 3H_2O$ (**1**). The formula of **1** was determined based on single-crystal X-ray diffraction analysis, element analysis, and thermogravimetric analysis. **1** can take over the chemical energy produced in the peroxyoxalate chemiluminescence (POCL) system and exhibits remarkable green light (E_m = 530 nm) emission, which makes it the first example of MOFs exhibiting direct CL emission. Additionally, **1** exhibits dual tunable fluorescence sensing behavior by tuning the excitation wavelength. When excited at 368 nm, **1** acts as "turn-off" sensor for electron-rich/deficient molecules, while "turn-on" sensing of electron-rich molecules can be achieved when the excitation wavelength was tuned to 200 nm.

Single-crystal X-ray diffraction analysis revealed that **1** crystallizes in the $P2_1/c$ space group. The fundamental asymmetric unit of **1** contains one **L** ligand, one cadmium(II) cation, and one coordinated DMF molecule. As shown in **Figure 1**, the carboxylate groups of the **L** ligand take two coordination modes: in the first mode, each carboxylate group of **L** coordinates to three Cd^{II} centers in mono- and bidentate fashion using its two carboxylate oxygen atoms, respectively; in the second mode, each carboxylate group of **L** coordinates to two Cd^{II} centers in bidentate fashion. The Cd^{II} cation coordinates to five carboxyl oxygen atoms from five **L** ligands and one DMF molecule. Further bridged by carboxylate groups, the hexa-coordinated Cd^{II} centers form infinite 1D rod-shaped metal-carboxylate secondary building units (SBUs), running along the *b*-axis. Each **L** ligand connects two different Cd-SBUs in a parallel way with the π–π distance of 3.487 Å, and each Cd-SBU connects with other four different SBUs by **L** linkers to form a 3D infinite framework with rhomboic 1D nanotubes propagated along the *b*-axis, and the vacancies are fully filled with DMF and water molecules.

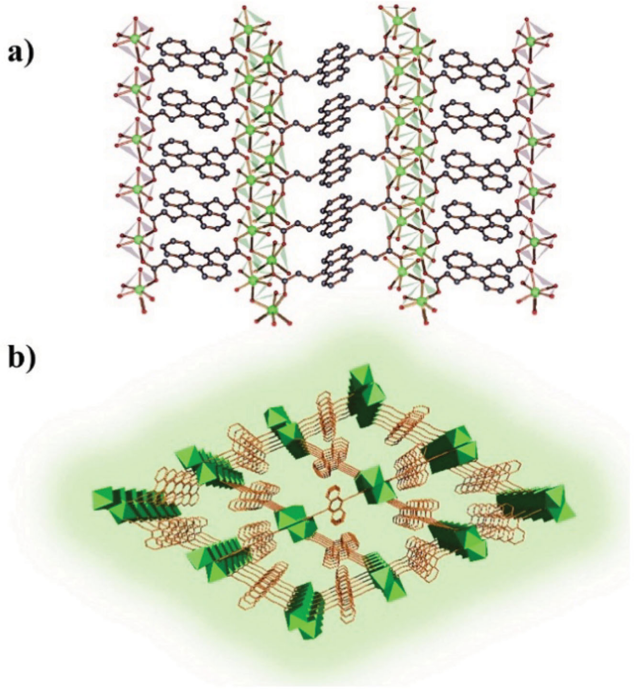

Figure 1. a) A side view of MOF **1**, showing the coordination mode of **L** ligands, the coordination environments of Cd^{II} ions, and the connection between the 1D rod-shaped Cd^{II}-carboxylate SBUs and **L** ligands. b) A perspective view of the 3D framework structure of **1** with 1D open-ended channel (DMF and H_2O molecules were emitted for clearance).

2.2. Chemiluminescence

To determine whether the selected ligand H_2**L** provides efficient contribution in building multiresponsive framework, the emission spectrum of **1** excited by chemical energy and light irradiation were studied. Traditional POCL system was selected to study the chemiluminescent behavior of **1**. It appeared quite bright to the naked eye when **1** was added to the POCL system (E_m = 530 nm, **Figure 2**). To thoroughly investigate the CL property of **1** in terms of intensity and lifetime, different POCL conditions were carried out and the results are listed in **Table 1**. Increasing the temperature and the concentration of bis[3,4,6-trichloro-2-(pentyloxycarbonyl)phenyl] oxalate (CPPO) and *tert* -BuOH led to the improvement both in intensity and lifetime (Table 1, entries 1–5), while over addition of reactants or too high reaction temperature resulted decay either in intensity or lifetime (Table 1, entries 6–9). The reason may be that under modest conditions the reaction was carried out in a controllable way, releasing the energy in a much more

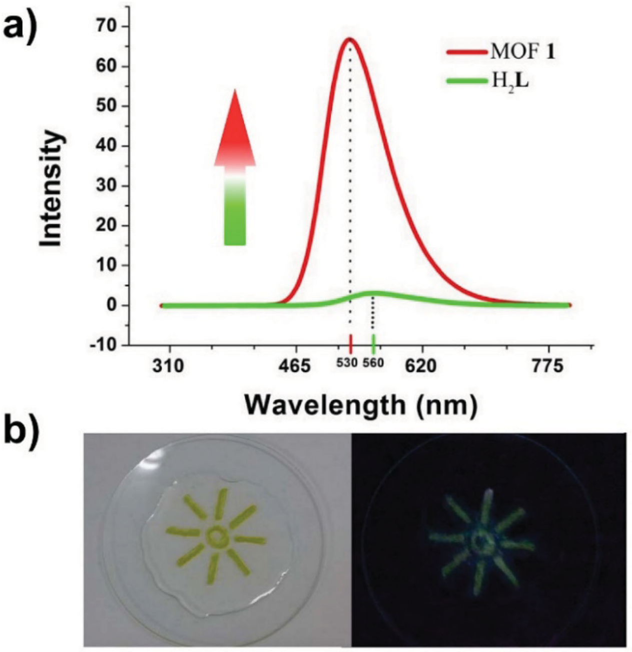

Figure 2. a) Chemiluminescence emission spectrum of **1** and H_2**L**. b) Photographs of **1** fixed on a watch glass by double-faced tape covered with the POCL reaction solution under ambient light (left) and in the dark (right), showing the direct CL emission.

Table 1. Results of the chemiluminescence study under different conditions.

Entry[a)]	CPPO [mg mL^{-1}]	Oxidant	T [°C]	*tert*-BuOH [%]	Intensity	Lifetime [min]
1	8	H_2O_2	35	4	4.461	70
2	14	H_2O_2	35	4	11.68	86
3	20	H_2O_2	35	4	66.73	180
4	20	H_2O_2	35	2	N.D.	N.D.
5	20	H_2O_2	15	4	11.03	480
6	28	H_2O_2	35	4	98.1	95
7	20	H_2O_2	35	8	1.916	60
8	20	H_2O_2	65	4	97.6	84
9	20	H_2O_2	80	4	1.45	21
10	20	TBHP[b)]	35	4	0.327	27
11	20	mCPBA[c)]	35	4	0.306	40
12	20	PhIO	35	4	N.D.	N.D.
13[d)]	20	H_2O_2	35	4	3.069	126
14[e)]	20	H_2O_2	35	4	63.27	160

[a)] Detailed procedure for CL study and the correlation between the emission intensity and reaction time for each entry are given in Supporting Information; [b)] *tert*-Butyl hydroperoxide, 70% aqueous solution; [c)] *m*-Chloroperoxybenzoic acid, 85% in purity; [d)] Free ligand H_2**L** (0.5 mg, 2 mol%) and $Cd(NO_3)_2 \cdot 4H_2O$ (0.5 mg, 2 mol%) were employed as the CL agent; [e)] The sixth cycle.

compatible level compared to that of harsh conditions for **1** to take over. **1** emitted green light under optimized condition with a maximum relative emission intensity of 66.73 and lifetime of ≈180 min (Table 1, entry 3).

Chemically initiated electron exchange luminescence (CIEEL) is believed and proved as the mechanism for the POCL process.[12] In our case, intermolecular CIEEL mechanism may be involved: 1,2-dioxetanedione generated from the reaction between the oxidant and CPPO interacts and exchanges electron with the anthracene ring located inside **1**, finally resulting excited **1*** accompanied the release of CO_2 (Figure S9, Supporting Information). The ligand H_2**L** exhibited similar chemiluminescent behavior (E_m = 560 nm, Figure 2). The observed blueshift (30 nm) and improvements of emission intensity and lifetime of **1** are probably attributed to the formation of 3D architecture, which leads to the reduction of nonradiative decay rate. **1** showed remarkable structural stability, powder X-ray diffraction (PXRD) analysis of the recovered sample indicated the structural integrity was maintained after six cycles (Table 1, entry 14; Figure S3, Supporting Information). Interestingly, only hydrogen peroxide can help to generate clear visible CL emission (Table 1, entries 10-12). The selectivity makes **1** a potential reusable visual sensor toward hydrogen peroxide.

2.3. Photoluminescence and Dual Switchable Sensing

The PL spectrum of **1** dispersed in DMF also exhibits strong fluorescence peaked at 515 nm, which originates from the ligand (π–π*, E_m = 532 nm; Figure S26, Supporting Information). The fluorescence of **1** dispersed in DMF showed strong "turn-off"-type responses when encountering different electron-deficient aromatics excited at 368 nm (Figures S27–S42, Supporting Information), and moderate quenching in intensity was observed when electron-rich aromatics were added (Figures S45–S50, Supporting Information). **Figure 3**a shows the reduction in fluorescence intensity and the linear quenching range of **1** dispersed in DMF upon adding nitrobenzene (NB). Quantitative detection of NB ranged from 200 to 800 ppm was established. Similarly, **1** presents remarkable capacity to detect nitroaromatics with different linear detection ranges through the "turn-off" effect (Figures S27–S42, Supporting Information). Besides quantity, **1** also presents remarkable sensitivity. When dispersed in 1 ppm DMF solution of quenchers, a maximum quenching efficiency of 14.8% was observed for 2,4-dinitrotoluene (Figure 3b).

Interestingly, "turn-on" response toward electron-rich aromatics was observed when excited at 200 nm, instead of the "turn-off" response observed upon excitation at 368 nm. The quenching efficiency of **1** for toluene is 21.2% when excited 368 nm, while a maximum of 20% enhancement of the fluorescence intensity was observed when excited at 200 nm (**Figure 4**a).

Dual response for a specific analyte is rare in the literature,[13] so some theoretical calculations have been carried out to study the reason. Because of the highly localized electronic states of those MOFs containing d^{10} metals, an idealized nonperiodic cluster ([**L**$_2$Cd$_2$(DMF]$_2$]) was built according to experimental data as the representative of **1** for further DFT calculation.[14] The results indicate that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **1** are mainly dominated by the ligand **L**, which is very similar to that of the free ligand H_2**L** (Figures S24 and S25, Supporting Information). The energy gap increases from 3.00 eV (H_2**L**) to 3.07 eV (**1**), and the difference relative to **1** (0.07 eV) is very close to the observed blueshift of the fluorescence (17 nm, 0.077 eV; Table S4, Supporting Information). The excited LUMO energy level of **1** is higher than that of the nitroaromatics, whereas lower than that of the electron-rich compounds, resulting different charge transfer pathways corresponding to different

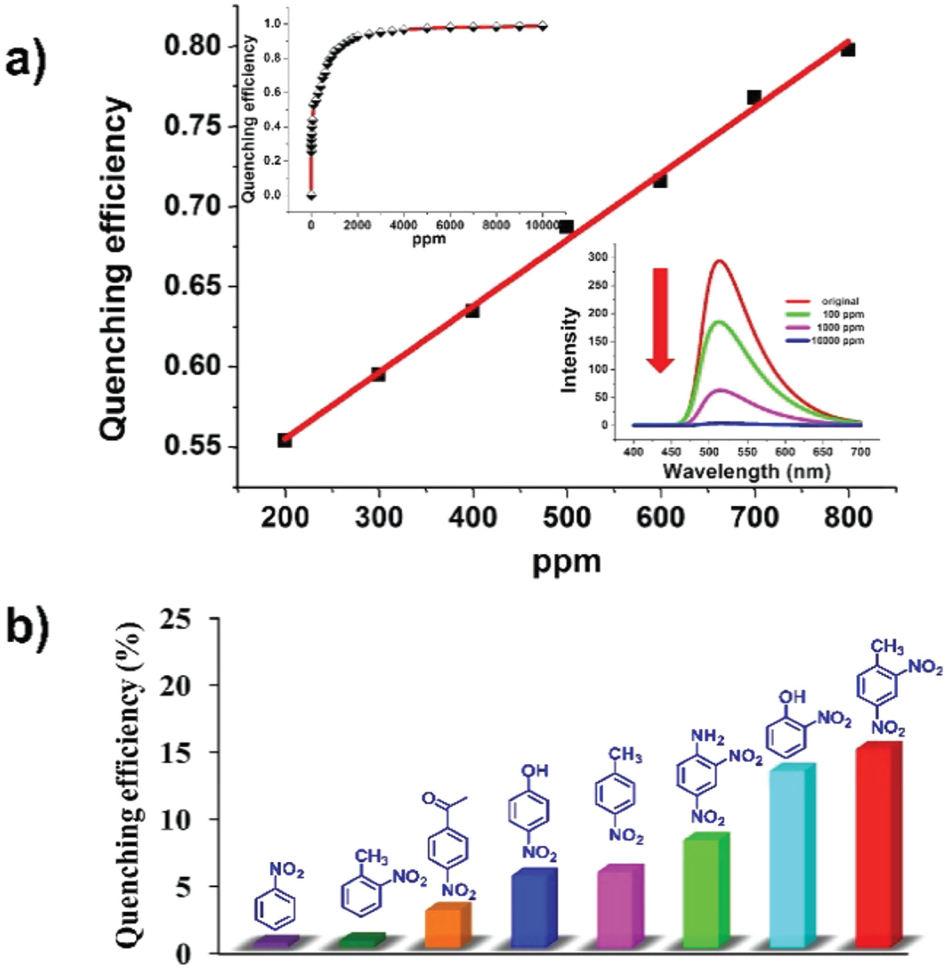

Figure 3. a) Linear quenching of **1** dispersed in DMF by gradual addition of NB. Inset: Quenching efficiency versus the concentration of NB (left); fluorescence emission spectrum of **1** dispersed in DMF solutions of NB with different concentrations (right). b) Reduction in fluorescence intensity (plotted as quenching efficiency) observed upon dispersing **1** in 1 ppm DMF solution of quenchers.

fluorescence response (**Figure 5**). The larger band gaps of those electronrich aromatics may be responsible for the dual sensing behavior of **1**. Those aromatics remained in the ground states when excited at 368 nm, which made it impossible for the occurrence of the expected charge transfer. Under such circumstances, the solvent cage effect dominated the fluorescence behavior of **1**. It is known that the excited states of conjugated aromatics have larger dipole moment than their ground states, indicating that solvent with larger polarity is more favorable. DMF has the largest polarity among the selected solvents, giving the strongest fluorescence emission (Figure S44, Supporting Information). Addition of the electron-rich aromatics may reduce the total polarity of the dispersing system, resulting quenching in fluorescence intensity (Figures S45–S50, Supporting Information). On the contrary, analyte of this group reached its excited states when excited at 200 nm, which opened the pathway of charge transfer from its LUMO to **1**. Fluorescence excitation spectrum of **1** can cover the entire range of the fluorescence emission of these pure aromatics (307–367 nm; Figures S51–S56, Supporting Information). The UV light emitted by these aromatics may be used as a second excitation source for **1**, resulting the observed fluorescence enhancement (Figures S57–S62, Supporting Information).

1 can be simply recovered by filtration, PXRD analysis of the recovered solid indicated the structural integrity was maintained. The recovered solid could be reused for a significant number of cycles after washed by DMF without deteriorating the sensing activity (Figure S43, Supporting Information). It is noteworthy that the quenching behavior implies high sensitivity and stability of the material for its long time quantitative detecting application.

4. Conclusion

In summary, a multiresponsive luminescent MOF **1** has been synthesized. **1** is the first example of direct chemiluminescent MOFs, which exhibits green light emission peaked at 530 nm when employed as CL agent for the POCL system. Besides, **1** exhibits novel dual tunable sensing property toward

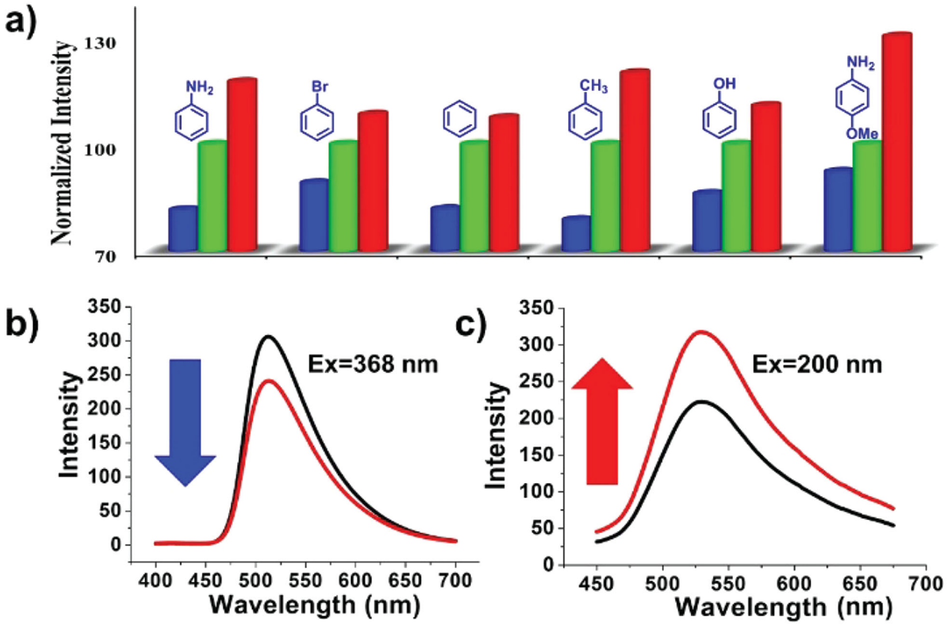

Figure 4. a) Change in fluorescence intensity upon dispersing **1** in DMF solutions of electron rich aromatics excited at different wavelengths: green bar represents the original normalized intensity; blue and red bars represent the fluorescence intensity of **1** dispersed in DMF solutions of electron-rich aromatics excited at 368 and 200 nm, respectively. b,c) Fluorescence "turn-off" and "turn-on" detections of **1** toward toluene excited at 368 and 200 nm, respectively.

electron-rich aromatics. "Turn-on" and "turn-off" detections can be simply switched by tuning the excitation wavelength. Additionally, **1** also presents remarkable capacity to quantitatively detect different nitroaromatics. The remarkable direct CL and PL properties of **1** indicate a step forward in multiresponsive sensors. Moreover, by employing various anthracene derivatives and metal sites, the resulting chemi/photoluminescent and structural properties of MOFs can be finely tuned, indicating a very promising strategy to develop multiresponsive luminescent sensors.

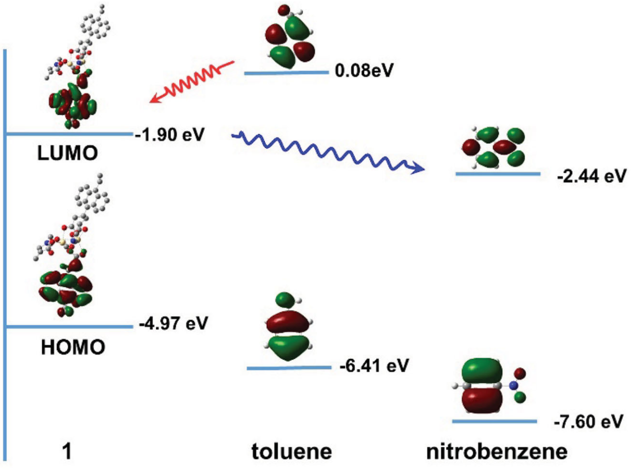

Figure 5. Schematic drawings of the electronic structures of **1**, toluene and NB, showing the possible pathway for charge transfer.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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