# Electronic Supplementary Information (22 pages)

## Triptycene based luminescent metal-organic gels for chemosensing

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#### Section S1 Materials and General Procedures

All solvents and reagents were purchased commercially and, unless otherwise noted, were used without further purification. Microanalyses were carried out at the Anorganisch-Chemisches Institut of the University of Zurich. FTIR spectra were obtained by using a Bio-Rad FTS-45 FTIR spectrometer. The powder XRD patterns were obtained with a Bruker D8 Advance system equipped with a Cu sealed tube ( $\lambda = 1.5406$  Å). The following conditions were applied: 40 kV, 40 mA, increment = 0.007°, scan speed = 1.5 s/step. The simulated powder pattern was calculated from the single crystal X-ray diffraction data and generated with Mercury 2.3 software. All TGA experiments were performed under a N<sub>2</sub> atmosphere from 25 - 800 °C at a temperature ramp rate of 1 °C/min. Scanning Electron Microscopy (SEM) was recorded in a JEOL, JMS-6700F, field emission scanning electron microscope. Rheology experiments were performed in an SDT Q series advanced rheometer AR 2000.

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### Section S2 Synthesis

Synthesis of 1,4,5,8-triptycenetetracarboxylic acid was accomplished according to the Scheme S1 following multi-step synthetic procedure reported in the literature.<sup>[S1,S2]</sup>



Scheme S1. Synthesis of 1,4,5,8-triptycenetetracarboxylic acid (H<sub>4</sub>*ttc*).

## Synthesis of Al-Gel G1.

Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.054 g, 0.144 mmol) and 1,4,5,8-triptycenetetracarboxylic acid (0.03 g, 0.069 mmol) were dissolved in 1 mL of DMF in a 2 mL glass vial. After capping tightly, the vial was heated to 125 °C at a rate of 2 °C/min for 5-20 h in an isothermal oven to yield the opaque Al-gel **G1** (Fig. S2).

Microanalysis of the xerogel (air dried gel), Found: C, 33.24; H, 5.68; N, 11.9%.



*Fig.* **S1.** The photo of as-prepared Al-gel obtained when the overall concetration (w/v) of 1.5 wt% (a), 2.5 wt% (b) and 5 wt% (c) (considering all the reactants) was employed.

## Synthesis of Cr-Gel G2.

 $Cr(NO_3)_3 \cdot 9H_2O$  (0.057 g, 0.135 mmol) and 1,4,5,8-triptycenetetracarboxylic acid (0.03 g, 0.069 mmol) were dissolved in 2 mL of DMF in a 4 mL glass vial. After capping tightly, the vial was heated to 125 °C at a rate of 2 °C/min for 5-20 h in an isothermal oven to yield the dark-green Cr-gel material **G2** (Fig. S2).

Microanalysis of the Cr-xerogel (air dried gel), Found: C, 33.48; H, 5.51; N, 11.55%.



*Fig.* **S2.** The photo of as-prepared Al-gel **G1** (a), Al-gel **G1** under uv lamp (b) and as-prepared Cr-gel **G2** (c) and Cr-gel **G2** under uv lamp (d).

### Synthesis of *trip*-MOF-1 [Co<sub>2</sub>(*ttc*)(DMF)(H<sub>2</sub>O)] (*ttc* = 1,4,5,8-triptycenetetracarboxylate).

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.020 g, 0.069 mmol) and 1,4,5,8-triptycenetetracarboxylic acid (0.020 g, 0.046 mmol) were dissolved in 0.6 mL of DMF in a 2 mL glass vial. After capping tightly, the vial was heated to 125 °C at a rate of 2 °C/min for 20 h in an isothermal oven. The vial containing dark purple crystals were removed from the mother liquor and washed with DMF (3 × 5 mL) [yield: 0.015 g, 51% based on 1,4,5,8-triptycenetetracarboxylic acid]. Elemental analysis calcd (%) for C<sub>27</sub>H<sub>19</sub>Co<sub>2</sub>NO<sub>10</sub> = [Co<sub>2</sub>(*ttc*)(DMF)(H<sub>2</sub>O)]: C 51.04, H 3.01, N 2.20; found C, 51.52; H, 3.12; N, 2.61.

### Section S3 Crystallographic Data

#### Single X-Ray Crystal Diffraction Studies on trip-MOF-1

Single-crystal X-ray diffraction data was collected at 183(2) K on a Xcalibur diffractometer (Agilent Technologies, Ruby CCD detector) using a single wavelength Enhance X-ray source with MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å.<sup>[S3]</sup> The selected suitable single crystal was mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, analytical absorption correction,<sup>[S4]</sup> and data reduction were performed with the Oxford program suite CrysAlisPro.<sup>[S3]</sup> The crystal structure was solved with SHELXS97<sup>[S5]</sup> using direct methods and was refined by full-matrix least-squares methods on F2 with SHELXL97.<sup>[S5]</sup> All programs used during the crystal structure determination process are included in the WINGX software.<sup>[S6]</sup> The program PLATON<sup>[S7]</sup> was used to check the result of the X-ray analysis.

CCDC 872964 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif

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	trip-MOF-1
empirical formula	C <sub>27</sub> H <sub>19</sub> Co <sub>2</sub> NO <sub>10</sub>
formula weight (g·mol <sup>-1</sup> )	635.29
temperature (K)	183(2)
wavelength (Å)	0.71073
crystal system, space group	Monoclinic, C 2/ c
<i>a</i> (Å)	17.1691(5)
<i>b</i> (Å)	11.0334(5)
<i>c</i> (Å)	16.3274(6)
α (°)	90
β (°)	98.302(3)
γ (°)	90
volume (Å <sup>3</sup> )	3060.5(2)
Z, density (calcd) (Mg·m <sup>-3</sup> )	4, 1.379
abs coefficient (mm <sup>-1</sup> )	1.135
<i>F</i> (000)	1288
crystal size (mm <sup>3</sup> )	0.23 x 0.08 x 0.02
θ range (°)	2.45 to 25.00
reflections collected	9118
reflections unique	2691 [ <i>R</i> (int) = 0.0246]
completeness to $\theta$ (%)	99.9
absorption correction	analytical
max/min transmission	0.975 / 0.864
data / restraints / parameters	1970 / 12 / 254
goodness-of-fit on $F^2$	1.107
final $R_1$ and $wR_2$ indices $[I > 2\sigma(I)]$	0.0756, 0.2135
$R_1$ and $wR_2$ indices (all data)	0.1048, 0.2256
largest diff. peak and hole (e.Å <sup>-3</sup> )	0.796, -0.728

The unweighted R-factor is  $R_1 = \sum (Fo - Fc) / \sum Fo$ ;  $I > 2\sigma(I)$  and the weighted R-factor is  $wR_2 = {\sum (Fo^2 - Fc^2)^2 / \sum w(Fo^2)^2}^{1/2}$ .

Section S4 Powder X-Ray Diffraction Patterns



*Fig.* **S3.** Powder X-ray diffraction patterns: simulated from the single crystal X-ray structure of *trip*-MOF-1 (black) and as-prepared *trip*-MOF-1 (red).

Section S5 IR Spectra



*Fig.* **S4.** FT-IR spectra of the xerogel of Al-gel **G1** (blue) and the ligand  $H_4ttc$  (red).



Fig. S5. FT-IR spectrum of as-prepared trip-MOF-1.

Section S6 Thermal Gravimetric Analysis



*Fig.* **S6.** TGA trace of xerogels (air dried) of as-prepared Al-gel **G1** (black) and as-prepared Cr-gel **G2** (red).

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*Fig.* **S7.** TGA trace of as-prepared *trip*-MOF-1.

#### Section S7 Photophysical Study

**Preparation of stock solutions:** In a typical preparation of stock solution for the Al-gel **G1** and Cr-gel **G2**, approximately 5 mg of as-prepared gel materials (or 0.20 mg of their corresponding xerogels) were suspended in 2 mL of ethanol and allowed to stir at room temperature for at least 20 hrs to give cloudy white and light green suspensions respectively. In the case of *trip*-MOF-**1**, the as-prepared MOF crystals (1 mg) were thoroughly washed with ethanol and solvent decanted. The crystals were then placed in an empty vial containing 5 mL of fresh ethanol which was then allowed to crush mechanically by vigorous stirring with a stir bar at room temperature for 20 hrs to generate a purple cloudy suspension of *trip*-MOF-**1**. The resulting suspension of gels/crystals were then carefully stored under sealed conditions.

The steady-state fluorescence spectra as well as the quenching experiments with different analytes were carried out by subsequently placing 2 mL of individual stock solutions in quartz cell of 1 cm width while stirring. All the titrations were carried out by gradually adding quenchers (analytes) (1 mM) solution in an incremental fashion. Their corresponding fluorescence emission spectra were recorded at 298 K. Each titration was repeated at least three times to get concordant value. For all measurements, dispersed solution of the receptors were

excited at  $\lambda_{ex} = 318$  nm and their corresponding emission wavelength was monitored from  $\lambda_{em} = 340$  nm to 580 nm.

For estimating the Stern-Volmer binding constant, exactly 2 mL of the above mentioned stock solution of the individual receptors were used for the titration. The emission intensity was recorded 10 minutes after the addition of the analytes under stirring conditions in order to ensure sufficient time for the diffusion of quenchers to the receptors.

The Stern-Volmer equation  $I_o/I = 1 + K_{sv}[Q]$ , where  $I_o$ , I are the fluorescence intensity before and after addition of the quencher,  $K_{sv}$  is the Stern-Volmer quenching rate constant and [Q] is the concentration of the quenchers, was used for the determination of the binding constant.



*Fig.* **S8.** Emission spectra of  $H_4ttc$  (red) dispersed in ethanol followed by addition of few drops of DMF (excited at 315 nm) and of ethanol dispersed Al-gel **G1** (black) (excited at 318 nm).



*Fig.* **S9.** Fluorescence titration of Al-gel **G1** dispersed in ethanol with the addition of different volume of 1 mM solution of nitromethane in ethanol.



*Fig.* **S10.** Fluorescence titration of Al-gel **G1** dispersed in ethanol with the addition of different volume of 1 mM solution of nitrobenzene in ethanol.



*Fig. S11.* Fluorescence titration of Al-gel **G1** dispersed in ethanol with the addition of different volume of 1 mM solution of *m*-dinitrobenzene in ethanol.



*Fig.* **S12.** Fluorescence titration of Al-gel **G1** dispersed in ethanol with the addition of different volume of 1 mM solution of *p*-nitrophenol in ethanol.



*Fig.* **S13.** Fluorescence titration of Al-gel **G1** dispersed in ethanol with the addition of different volume of 1 mM solution of *m*-nitrophenol in ethanol.



*Fig.* **S14.** Fluorescence titration of Al-gel **G1** dispersed in ethanol with the addition of different volume of 1 mM solution of 2,4-dinitrophenol in ethanol.



*Fig.* **S15.** Fluorescence titration of Al-gel **G1** dispersed in ethanol with the addition of different volume of 1 mM solution of 2,6-dinitrophenol in ethanol.



*Fig.* **S16.** Fluorescence titration of Al-gel **G1** dispersed in ethanol with the addition of different volume of 1 mM solution of 2,4-dinitrotoluene (2,4-DNT) in ethanol.



*Fig.* **S17.** Fluorescence titration of Al-gel **G1** dispersed in ethanol with the addition of different volume of 1 mM solution of picric acid in ethanol.



*Fig.* **S18.** Fluorescence titration of Al-gel **G1** dispersed in ethanol with the addition of various concentration of PA.



*Fig.* **S19.** Fluorescence titration of  $H_4ttc$  suspended in ethanol with the addition of various concentration of PA (excited at 315 nm).



*Fig.* **S20.** Fluorescence titration of Al-gel **G1** dispersed in ethanol with the addition of various concentration of 2,4-DNT.



**Fig. S21.** Emission spectra of ethanol dispersed Cr-gel G2 (red) and *trip*-MOF-1 (black) (excited at 318 nm).



*Fig.* **S22.** Fluorescence titration of *trip*-MOF-1 dispersed in ethanol with the addition of various concentration of PA.



*Fig.* **S23.** Fluorescence titration of Cr-gel **G2** dispersed in ethanol with the addition of various concentration of PA.



*Fig.* **S24.** The Stern-Volmer plots for the titration of Cr-gel **G2** (dark cyan square) and *trip*-MOF-1 (red circle) with PA.

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*Fig.* **S25.** Reproducibility of the quenching ability of *trip*-MOF-1 (left) and Cr-gel **G2** (right) dispersed in ethanol to picric acid (PA) solution. The materials were recovered by centrifuging after each experiment and washed several times (4-5) with ethanol. The black bars (for both the materials) represent the initial fluorescence intensities where as the corresponding dark cyan and pink bars represent the intensities of *trip*-MOF-1 and Cr-gel **G2** after the addition of 100  $\mu$ L (1 mM) of a solution of PA, respectively.

### Solid state fluorescence study

Saturated vapour of nitrobenzene (NB), 2,4-dinitrotoluene (2,4-DNT), and picric acid (PA) were generated by keeping the analyte compounds in a sealed tube for three days to ensure that the equilibrated vapour pressure is reached. The solid state fluorescence quenching study was carried out by keeping the quartz plate coated with a thin film of Al-xerogel (prepared by smearing the as-prepared Al-gel **G1** in quartz plate followed by drying in air for 24 h at room temperature) in sealed tubes containing analytes for specific time. The fluorescence spectra of the exposed films (Fig. S26) were recorded immediately after taking out from the sealed tube without any delay.



*Fig.* **S26.** The time dependent emission spectra of Al-gel **G1** thin film upon exposure to saturated vapors of nitro benzene (a), 2,4-DNT (b) and PA (c). Plot of the solid state fluorescence quenching efficiency of NB (d, black), 2,4-DNT (d, dark cyan) and PA (d, red) at different time (sec) interval.

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### Section S8 Computational Data

To gain deeper understanding for the superior quenching of the luminescence intensity of Al-gel **G1** by PA over 2,4-DNT (reflected by the relatively high Stern-Volmer binding constant determined for PA), we resorted to perform density functional theory (DFT) calculations at the B3LYP/6-31G(d) level (Fig. S27). For simplicity we used discrete ligand (H<sub>4</sub>*ttc*) as model compound. The calculation indeed revealed that the LUMO energy of PA (-3.89 eV) is much lower than that of 2,4-DNT (-2.97 eV) with respect to the LUMO energy of H<sub>4</sub>*ttc* (-1.85 eV) favouring strong electron transfer in the case of PA.



**Fig. S27.** HOMO (left, bottom) and LUMO (left, top) of  $H_4ttc$  and the energy levels (right) calculated for  $H_4ttc$ , PA and DNT at the B3LYP/6–31G(d) level of theory with Gaussian09<sup>[S8]</sup>.

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