## Fluorescence-based detection of nitroaromatics by a luminescent second sphere adduct self-assembled by charge assisted hydrogen bonds.

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**Figure S11.** The luminescence titration results of **1** in the presence of nitrobenzene can be treated with the Stern–Volmer equation, F0/F = 1 + Ksv[Q], where Ksv is the quenching constant, and Q is the quencher concentration. F0 and F are the fluorescence intensities before and after the addition of analytes.

**Figure S12.** The luminescence titration results of **1** in the presence of 2–nitrotoluene can be treated with the Stern–Volmer equation, F0/F = 1 + Ksv[Q], where Ksv is the quenching constant, and Q is the quencher concentration. F0 and F are the fluorescence intensities before and after the addition of analytes.

**Figure S13.** The luminescence titration results of **1** in the presence of 3–nitrotoluene can be treated with the Stern–Volmer equation, F0/F = 1 + Ksv[Q], where Ksv is the quenching constant, and Q is the quencher concentration. F0 and F are the fluorescence intensities before and after the addition of analytes.

#### 1. Materials and methods

All chemicals were commercially purchased and used as received.

X-Ray powder diffraction (XRPD) patterns were recorded on a Bruker D8 reflection diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator.

IR spectra were obtained with Perkin Elmer 100 FT-IR spectrometer using KBr pellets.

<sup>1</sup>H NMR spectra were recorded on a Mercury-Plus 300 spectrometer (VARIAN, 300MHz) at 25°C with TMS as the internal reference.

#### 2. Fluorescence measurements

Solid-state emission spectra were recorded for the solid samples which were loaded into a sample cell (1 cm diameter) which was then fixed on a bracket at room temperature with Hitachi F-7000 fluorescence spectrophotometer. The excitation and emission slits used for the measurement of the solid state of the crystals were 5 nm wide, the scan speed was 1200 nm/min, and the scan voltage was 700V. Excitation wavelength was 285 nm and fluorescence emission was monitored from 300 nm to 550 nm.

#### 3. X-ray Crystallography

Crystals were performed on a Bruker P4 diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were determined using direct methods and refined (based on F2 using all independent data) by full-matrix least-square methods (SHELXTL 2014). Data were reduced by using the Bruker SAINT software. All non-hydrogen atoms were directly located from different Fourier maps and refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters.

#### 4. Synthesis of ligand L

4,4'-methylenebis(2,6-diethylaniline) (2.5 g, 0.008 mol) was slowly added into the solution of 5.0 g K<sub>2</sub>CO<sub>3</sub> and 30 ml CH<sub>3</sub>CN. 1-chloromethyl naphthalene (2.6 ml, 0.016 mol) was then continuously (2-3 drops/s) added into the mixture solution. After the reaction was heated to 83°C and stirred for 24 h, the mixture was cooled to room temperature. The reaction product was dissolved in CH<sub>3</sub>CN, and then washed with ethanol. Recrystallization using CH<sub>3</sub>CN and drying in vacuum produced white crystals: 3.4g, yield 70%. m.p. 137-138 °C IR(KBr),  $\lambda_{max}$  /

cm<sup>-1</sup>: 3352.15 cm<sup>-1</sup> (N<sup>+</sup>H), 3040.77 cm<sup>-1</sup> (Ar), 2964.09 cm<sup>-1</sup>, 1596.84 cm<sup>-1</sup>, 1508.64 cm<sup>-1</sup> (Ar), 1394.93 cm<sup>-1</sup> (C-N), 849.56 cm<sup>-1</sup> (Ar); <sup>1</sup>H NMR (DMSO, 300 MHz) δ: 1.09-1.14 (12H, t, CH<sub>3</sub>), 2.55-2.63 (8H, q, CH<sub>2</sub>), 3.75 (2H, s, CH<sub>2</sub>), 3.80-3.85 (2H, q, NH), 4.43-4.45 (4H, d, CH<sub>2</sub>), 6.89 (4H, s, Ar-H), 7.47- 8.14 (14H, m, Ar-H).

#### Single crystal X-ray structure of L.

The crystal structure of **L** comprises half molecule in the asymmetric unit, crystalizing in the C2/c monoclinic space group. There are weak interactions of the type C-H··· $\pi$  among the methylene groups and the benzene rings in adjacent molecules (Figure S1).



**Figure S1.** (a) Single crystal structure of L, (b) Side view showing the short  $C-H\cdots\pi$  contacts among adjacent molecules in L. (c) Crystal packing of L viewed along the *b*-crystallographic axis.



Figure S2. Simulated XRPD patter of L.

# 5. Preparation of chlorinated salt of [2HL]2Cl·2MeOH (L') and single crystal X-ray crystal structure.

L (0.02 g, 0.039 mol), 5 ml dichloromethane, 5 ml methanol and 2 drops concentrated HCl were placed in a 50 ml Erlenmeyer flask and shaken until the contents were dissolved. The flask was allowed to stand for 2-3 days at room temperature. Recrystallisation produced colorless granular crystals suitable for single crystal X-ray diffraction. Crystallographic analysis shows that the crystal has the formula [2HL]2Cl·2MeOH. In the asymmetric unit there is one diprotonated cation, two Cl<sup>-</sup> anions and two methanol molecules. Charge assisted hydrogen bond among the Cl<sup>-</sup> anions and the [2HL]<sup>2+</sup> cations lead to the extension of one dimensional chains (Figure S3b). Methanol is also included in the structure forming short contacts with the Cl<sup>-</sup> anion that do not form channels and.



**Figure S3**. (a) Single crystal structure of the chloride salt L', [H2L]2Cl·2MeOH. (b) Hydrogen bonding and (c) packing in [H2L]2Cl·2MeOH.



Figure S4. Simulated XRPD pattern of [2HL]2Cl·2MeOH (L').

## 6. Synthesis and single crystal structure of second sphere coordination adducts 1-3

### Preparation of [H<sub>2</sub>L]<sup>2+</sup>·[CdCl<sub>4</sub>]<sup>2-</sup>(crystal 1)

L (0.02 g, 0.039 mol), 5 ml dichloromethane,  $CdCl_4$  (0.015 g, 0.078 mol), 5 ml methanol and 2 drops concentrated hydrochloric acid were placed in a 50ml Erlenmeyer flask and shaken until the contents were dissolved. The flask was allowed to stand for 2-3 days at room temperature. Recrystallisation produced colorless granular crystals, m.p. 221-222°C.



Figure S5. (a) Simulated PXRD pattern of crystal 1 (b) Experiment PXRD pattern of crystal 1.

## Preparation of [H<sub>2</sub>L]<sup>2+</sup>·[CoCl<sub>4</sub>]<sup>2-</sup>(crystal 2)

L (0.02 g. 0.039 mol), 5 ml dichloromethane,  $CoCl_2 \cdot 6H_2O$  (0.016 g, 0.078 mol), 5ml methanol and 2 drops concentrated hydrochloric acid were placed in a 50ml Erlenmeyer flask and shaken until the contents were dissolved. The flask was allowed to stand for over 2 days at room temperature. Recrystallisation produced blue block crystals, m.p.213-215°C.



Figure S6. (a) Crystal structure of corresponding to second sphere adduct 2 showing the 1D ribbons formed by the hydrogen bonding among the metal ions and the cations. (b) Packing of 2.



Figure S7. (a) Simulated PXRD pattern of crystal 2 (b) Experiment PXRD pattern of crystal 2.

## Preparation of [H<sub>2</sub>L]<sup>2+</sup> [CuCl<sub>4</sub>]<sup>2-</sup>(crystal 3)

L (0.02 g, 0.039 mol), 5 ml dichloromethane,  $CuCl_2 \cdot 2H_2O$  (0.012 g 0.078 mol), 5 ml methanol and 2 drops concentrated hydrochloric acid were placed in a 50ml Erlenmeyer flask and shaken until the contents were dissolved. The flask was allowed to stand for over 1 day at room temperature. Recrystallisation produced yellow block crystals, m.p. 179-180°C.



**Figure S8**. (a) Crystal structure of corresponding to second sphere adduct **3** showing the 1D ribbons formed by the hydrogen bonding among the metal ions and the cations. (b) Packing of **3**.



Figure S9. (a) Simulated PXRD pattern of crystal 3 (b) Experiment PXRD pattern of crystal 3.

## Photoluminiscent measurements of [H<sub>2</sub>L]<sup>2+</sup> [CdCl<sub>4</sub>]<sup>2-</sup>(crystal 1)

To perform the PL experiments, 4.3 mg of crystal **1** was grinded, and then immersed in 10 mL EA ( $c = 5 \times 10-4$  mol/L). After treated by ultrasonication for 10 minutes, the sample was suspended in EA, giving rise to a suspension (Figure S10a). Then, 3 ml of the above solution were added to the cuvette (Figure S10b). The addition of 1000 ppm nitrobenzene (NB), 2-

nitrotoluene, 3-nitrotoluene, cyclohexane (CYH), ethyl acetate (EA), dimethylformamide (DMF), dioxane (Diox), iso-Propyl alcohol (IPA), dichloromethane (DCM), acetonitrile (CH3CN), Petroleum ether (PE) and even other non-nitroaromatic solvents such as benzene (PhH) and toluene (MB) in the cuvette. The emission intensity showed photoluminescence regions: 300-450 nm.

The sample after the photoluminescence experiments were recovered by filtration as shown in Figure S10.



Figure S10. Pictures showing the preparation of the suspension containing 1 in ethyl acetate.

Caculation of the Ksv using 1 in the presence of nitrobenzene, 2nitrotoluene and 3-nitrotoluene.



**Figure S11.** The luminescence titration results of **1** in the presence of nitrobenzene can be treated with the Stern–Volmer equation, F0/F = 1 + Ksv[Q], where Ksv is the quenching constant, and Q is the quencher concentration. F0 and F are the fluorescence intensities before and after the addition of analytes.



**Figure S12.** The luminescence titration results of **1** in the presence of 2–nitrotoluene can be treated with the Stern–Volmer equation, F0/F = 1 + Ksv[Q], where Ksv is the quenching constant, and Q is the quencher concentration. F0 and F are the fluorescence intensities before and after the addition of analytes.



**Figure S13.** The luminescence titration results of **1** in the presence of 3–nitrotoluene can be treated with the Stern–Volmer equation, F0/F = 1 + Ksv[Q], where Ksv is the quenching constant, and Q is the quencher concentration. F0 and F are the fluorescence intensities before and after the addition of analytes.