Electronic Supplementary Material (ESI) for New Journal of Chemistry.

A Luminescent Inorganic-Organic hybrid, [Cd($C_{16}H_{10}N_2O_8S$)(H_2O)], for the Selective and Recyclable Detection of Chromates and Dichromates in Aqueous Solution

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Electronic Supporting Information

Table S1. Selected bond distances and angles observed in [Cd(H_2L)(H_2O)], **1**.

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Bond	Distances (Å)	Angle	Amplitude (°)
Cd(1)-O(2)	2.338(3)	O(5)#1-Cd(1)-O(3)#2	97.12(12)
Cd(1)-O(9)	2.289(3)	O(5)#1-Cd(1)-O(9)	93.35(12)
Cd(1)-O(5)#1	2.229(3)	O(3)#2-Cd(1)-O(9)	104.12(11)
Cd(1)-O(3)#2	2.261(3)	O(5)#1-Cd(1)-O(4)#3	162.87(11)
Cd(1)-O(4)#3	2.327(3)	O(3)#2-Cd(1)-O(4)#3	84.49(10)
Cd(1)- O(6)#5	2.400(3)	O(9)-Cd(1)-O(4)#3	102.83(11)
O(3)-Cd(1)#4	2.261(3	O(5)#1-Cd(1)-O(2)	81.46(11)
O(4)-Cd(1)#5	2.327(3)	O(3)#2-Cd(1)-O(2)	97.66(11)
O(5)-Cd(1)#6	2.229(3)	O(9)-Cd(1)-O(2)	158.09(10)
O(6)-Cd(1)#5	2.400(3)	O(4)#3-Cd(1)-O(2)	81.42(11)
		O(5)#1-Cd(1)-O(6)#3	105.92(11)
		(3)#2-Cd(1)-O(6)#3	154.49(10)
		O(9)-Cd(1)-O(6)#3	85.58(10)
		O(4)#3-Cd(1)-O(6)#3	70.27(10)
		O(2)-Cd(1)-O(6)#3	75.55(10)

Symmetry transformations used to generate equivalent atoms: #1: -x+3/2,-y+1,z-1/2; #2: x-1,y,z; #3: x-1/2,-y+1/2,-z+1; #4: x+1,y,z; #5: x+1/2,-y+1/2,-z+1; #6: -x+3/2,-y+1,z+1/2.

Table S2. Hydrogen bonding interactions found in the crystal structure of **1**.

Interactions	D···A (Å)	H···A (Å)	D–H···A (deg)	Symmetry Code
O(9)–H(9B)···O(1)	2.734(5)	1.85(3)	173(3)	1-x,-1/2+y,1/2-z
O(9)–H(9A)···O(6)	3.035(4)	2.16(3)	166(2)	3/2+x,3/2-y,-z
N(2)–H(2)···O(9)	3.190(5)	2.53(3)	146(3)	3/2-x,2-y,-1/2+z

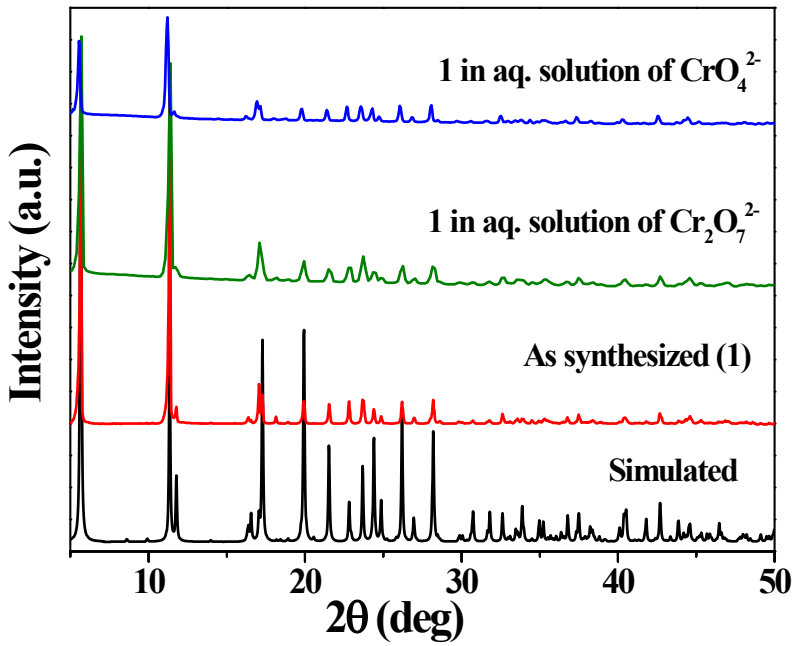


Fig. S1. PXRD patterns of compound **1**, simulated, as synthesized and after sensing of $Cr_2O_7^{2-}$ and CrO_4^{2-} in aqueous solutions.

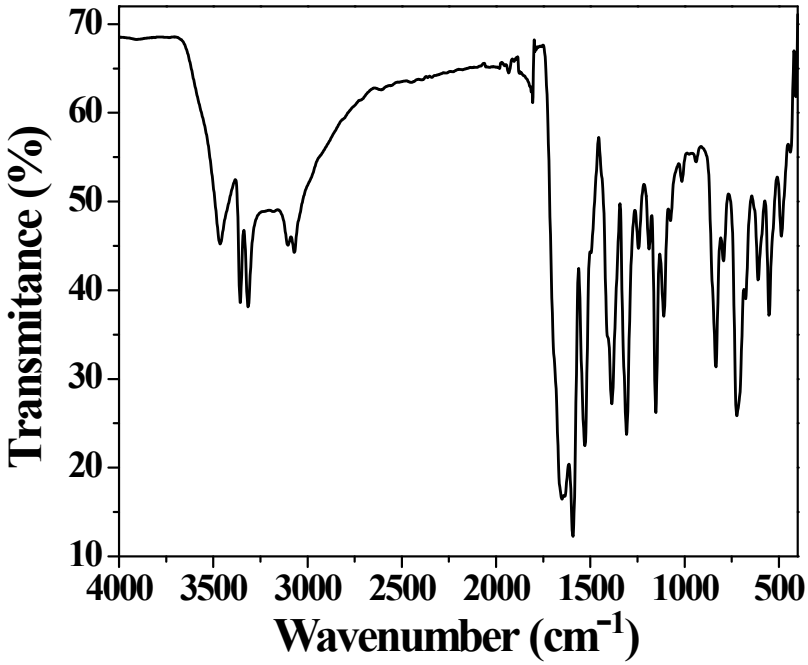


Fig. S2. IR spectra of the compound **1**

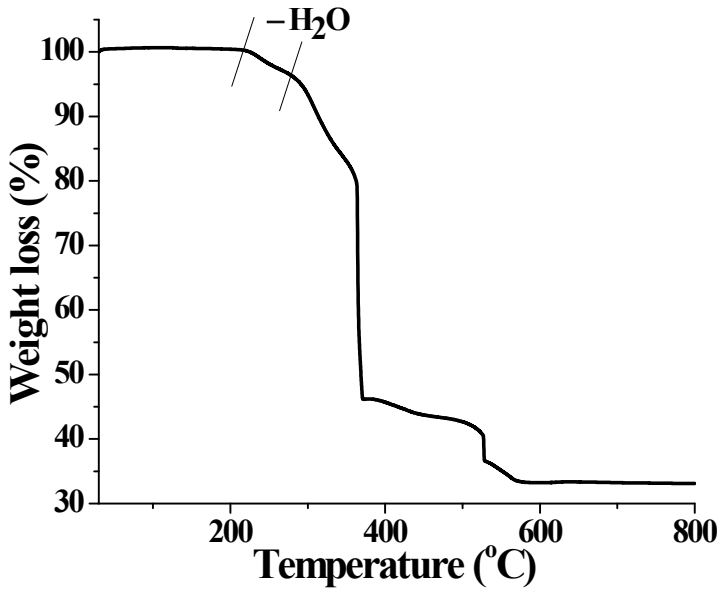


Fig. S3. TGA of compound 1

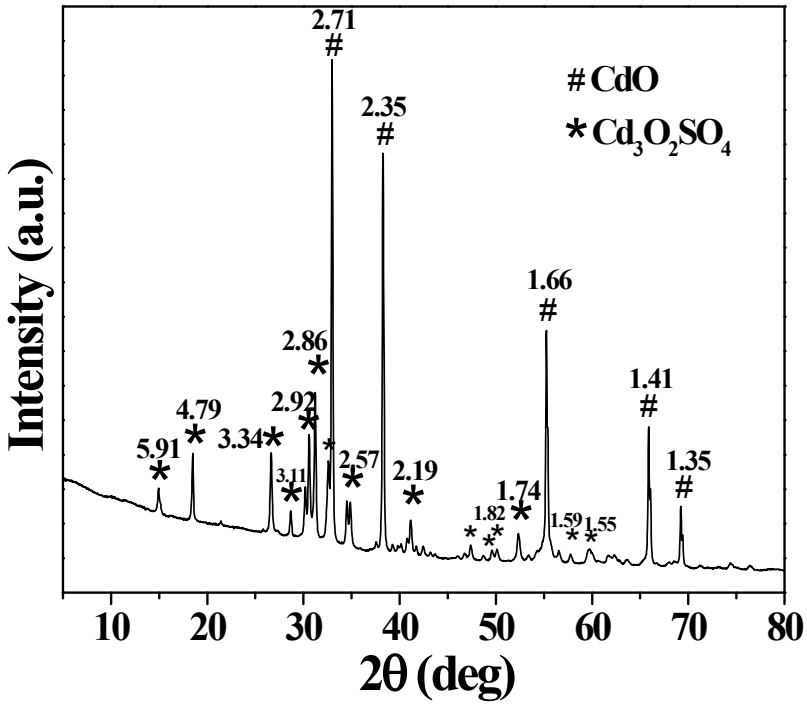


Fig. S4. Powder XRD pattern of the final product of compound **1** after TGA analysis. The numbers denote the d spacing of the peaks.

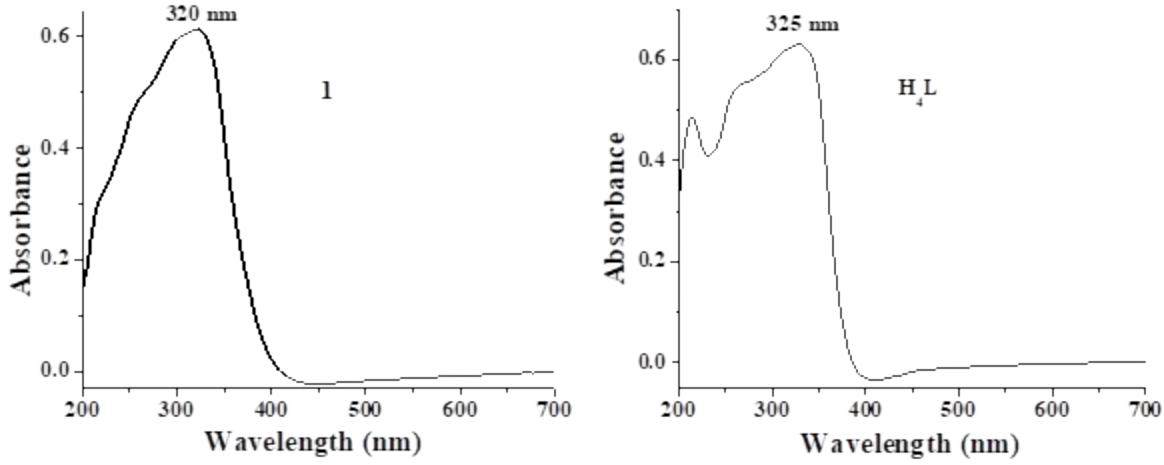


Fig. S5. The solid state UV□Vis absorption spectra of compound 1 and free ligand H4L.

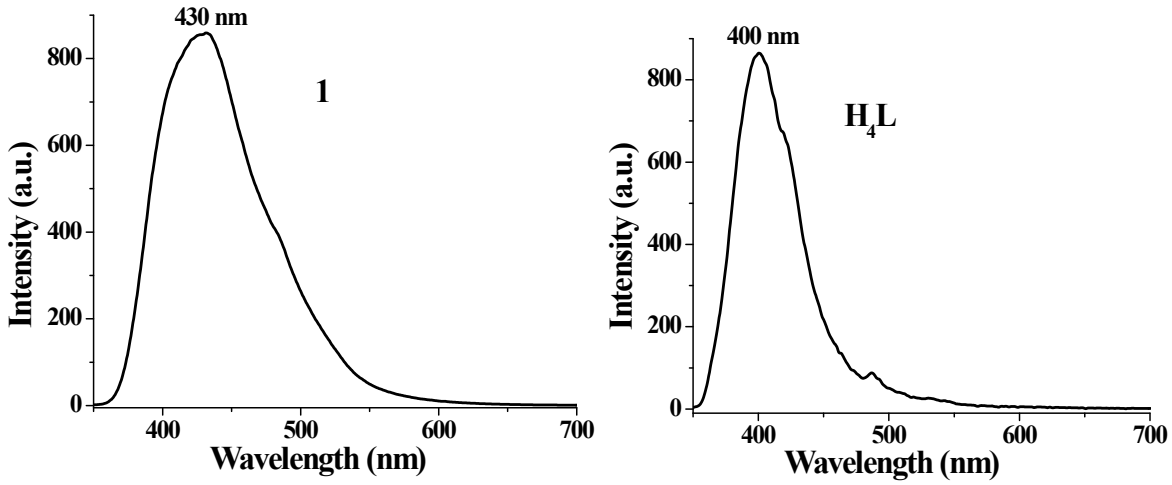


Fig. S6. Room temperature solid−state photoluminescence spectra of compound **1** and free ligand H_4L, λ_{ex} = 320 nm.

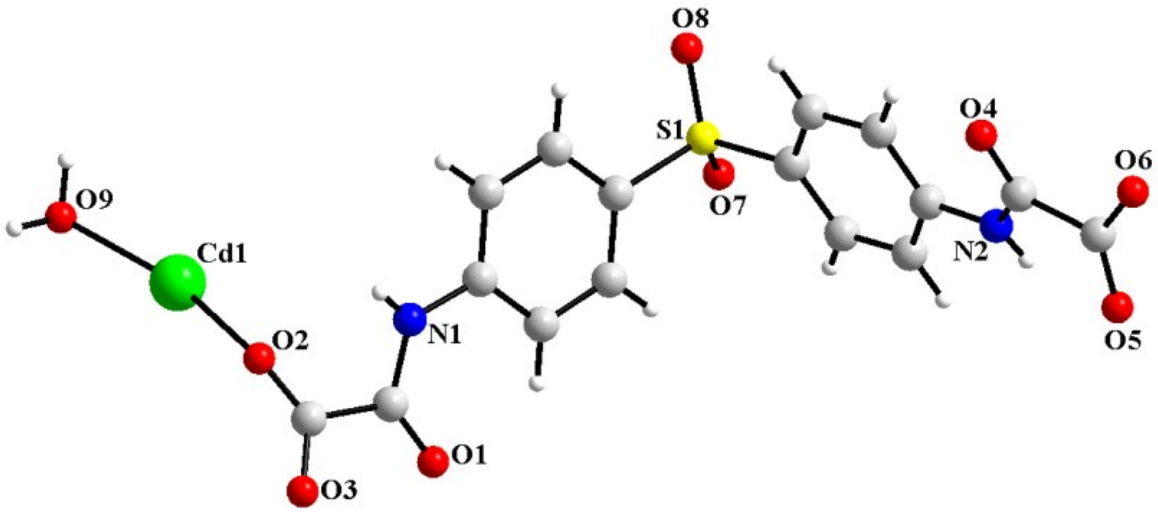


Fig. S7. The assymetric unit of compound 1.

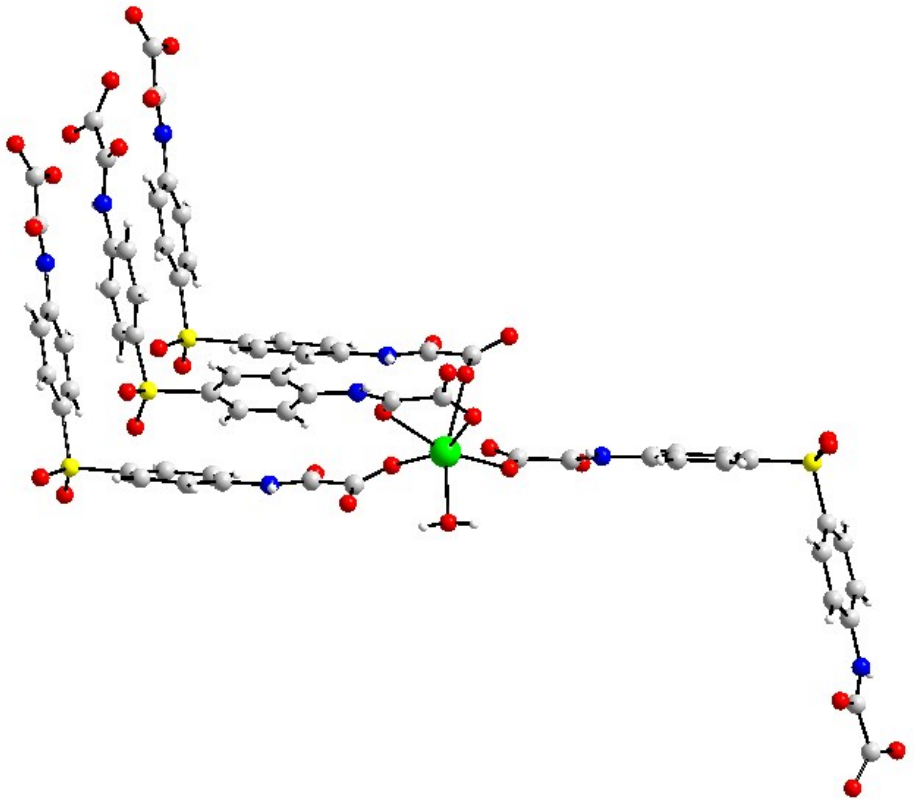


Fig. S8. Coordination environment of Cd^{2+} ion in compound **1**.

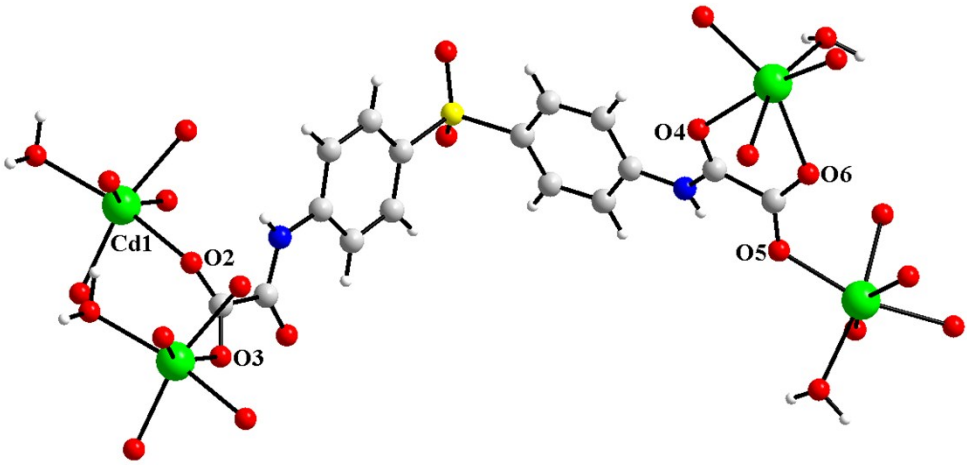


Fig. S9. Different connectivity of the two oxamato groups of H_2L^{2-} with Cd^{2+} ions in **1**.

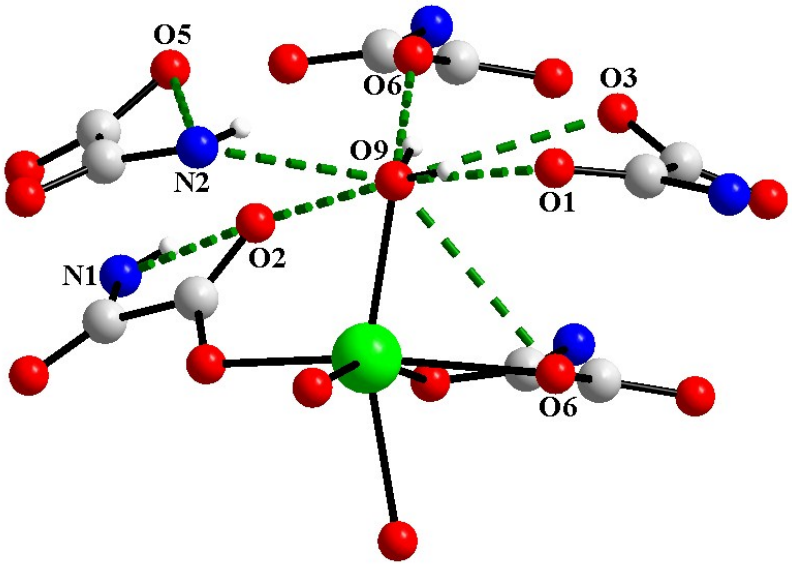


Fig. S10. Hydrogen bonding interactions between the coordinated water, N–H group and oxygen atoms of oxamato groups of the ligand in compound **1**.

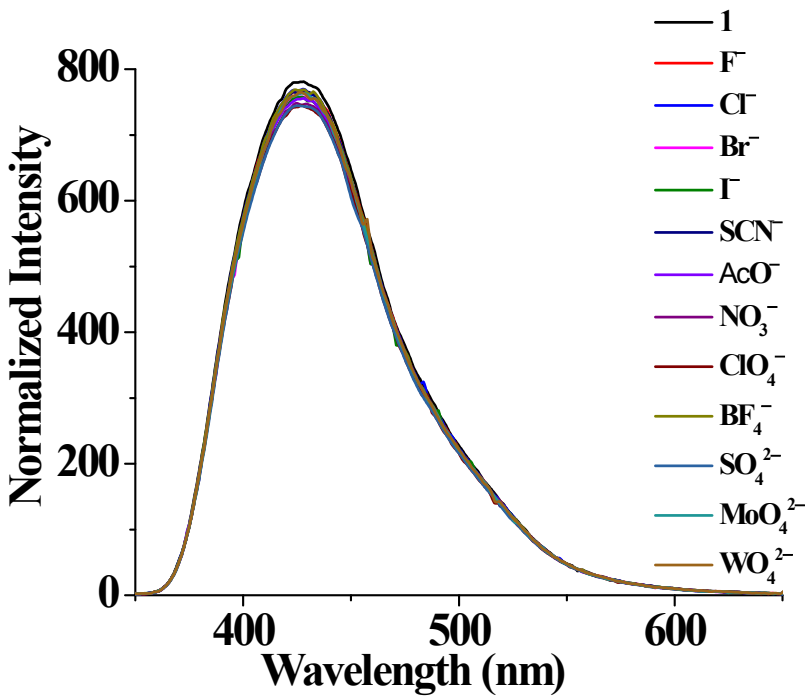


Fig. S11. The luminescence intensity of compound **1** in presence of different anions.

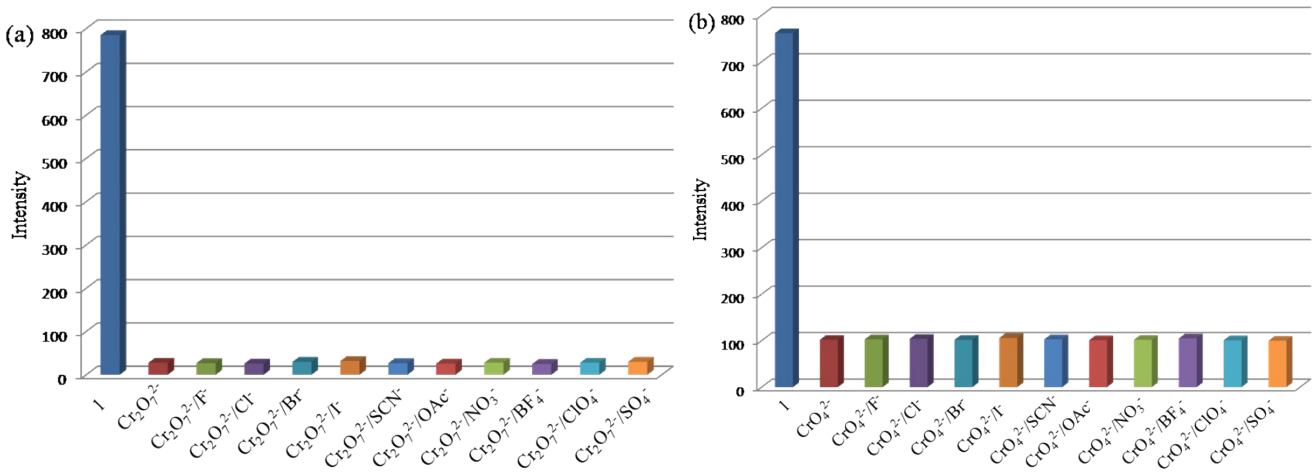


Fig. S12. Comparison of the luminescence quenching effect of (a) $Cr_2O_7^{2-}$ and (b) CrO_4^{2-} on compound **1** is presence of other competitive anions (10 x 10^{-4} M).

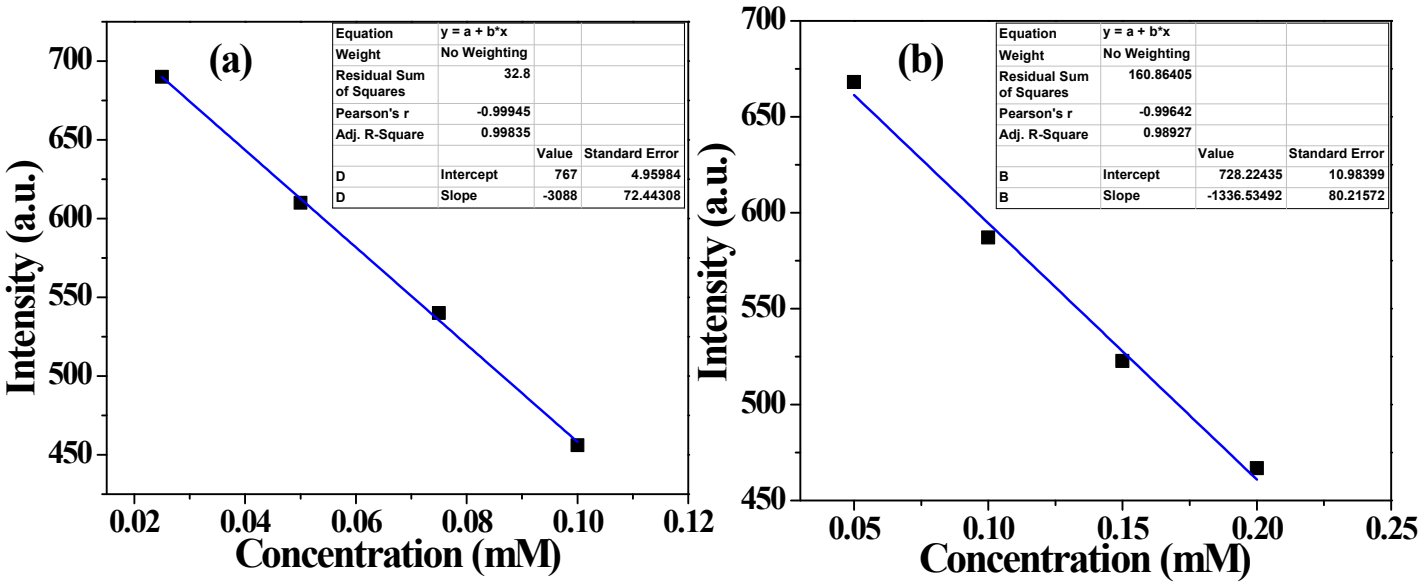


Fig. S13. Linear region of luminescence intensity of compound **1** upon addition of (a) $Cr_2O_7^{2-}$ and (b) CrO_4^{2-} solutions at λ_{em}=426 nm (λ_{ex} = 320 nm).

Detection Limit Calculation:

The luminescence intensity of the compound was plotted as a function of anion concentration. The limit of detection (LOD) is given by: LOD = 3σ/m, where σ is the standard deviation of the blank measurements without adding the anion and m is the slope of the linear plot.

Table S3. Standard deviation and detection limit calculation for $Cr_2O_7^{2-}$

Blank readings of **1** (without analyte)	Luminescence intensity
Reading 1	782.7
Reading 2	780.5
Reading 3	783.8
Reading 4	784.2
Reading 5	781.3
Standard Deviation (σ)	1.58

Slope from the graph (m)	3088 mM^{-1}
Detection limit (3σ/m)	0.00153 mM
Limit of detection (LOD)	0.45 ppm

Table S4. Standard deviation and detection limit calculation for CrO_4^{2-}

Blank readings of **1** (without analyte)	Luminescence intensity
Reading 1	760.5
Reading 2	761.6
Reading 3	763.4
Reading 4	762.3
Reading 5	759.2
Standard Deviation (σ)	1.62

Slope from the graph (m)	1336.5 mM^{-1}
Detection limit (3σ/m)	0.00364 mM
Limit of detection (LOD)	0.70 ppm

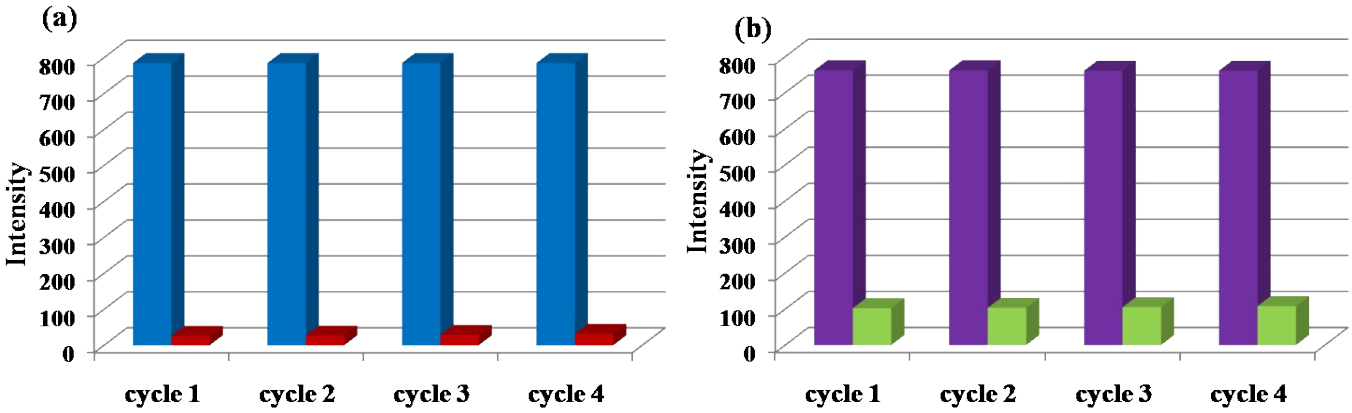


Fig. S14. Recyclability of compound **1** – as a sensor with $Cr_2O_7^{2-}$ (a) and CrO_4^{2-} (b). The intensity is measured at 426 nm (λ_{ex} = 320nm) for **1** and in presence of 10 x 10^{-4} M anion solutions.

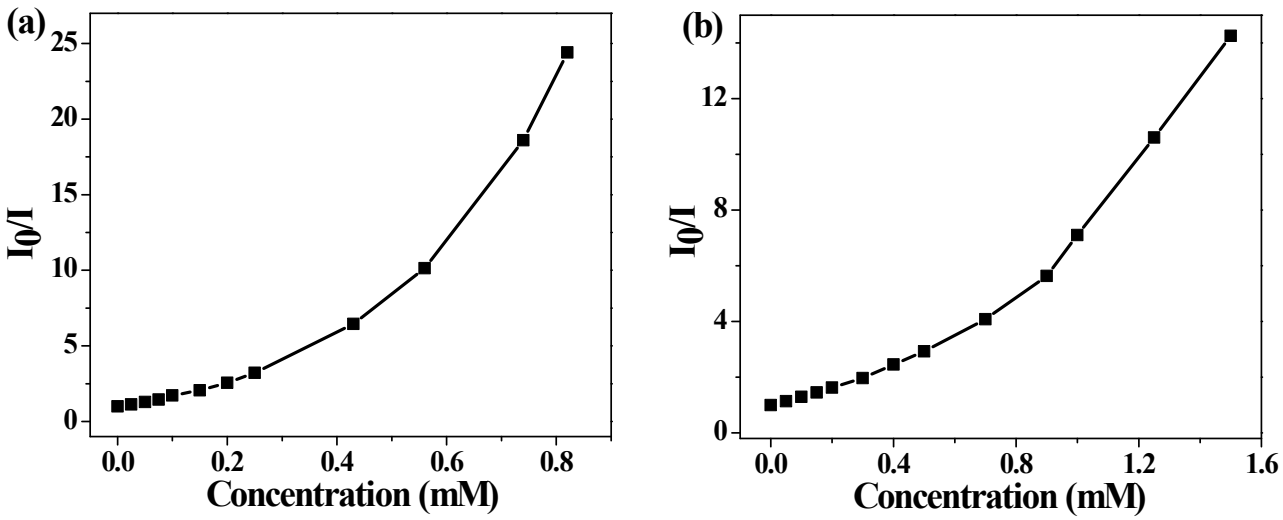


Fig. S15. Stern-Volmer plots for **1** at high concentration of (a) $Cr_2O_7^{2-}$ and (b) CrO_4^{2-}.

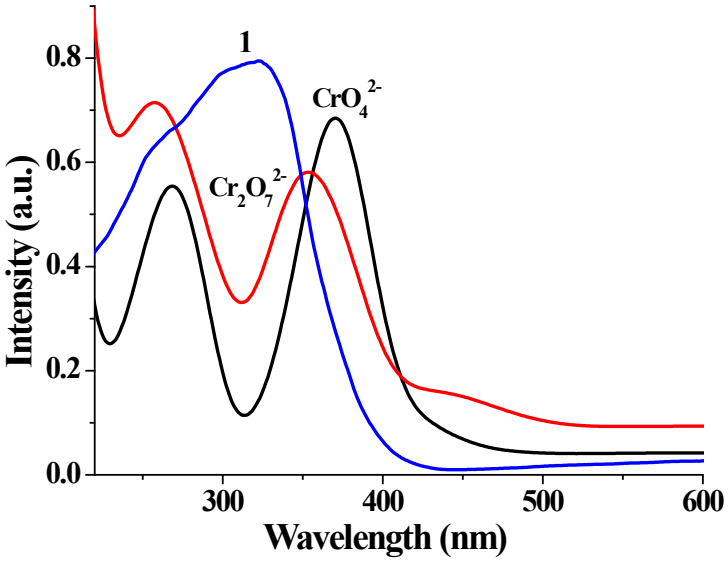


Fig. S16. Overlap between the absorption bands of $Cr_2O_7^{2-}$ and CrO_4^{2-} with the absorption spectra of compound **1**.

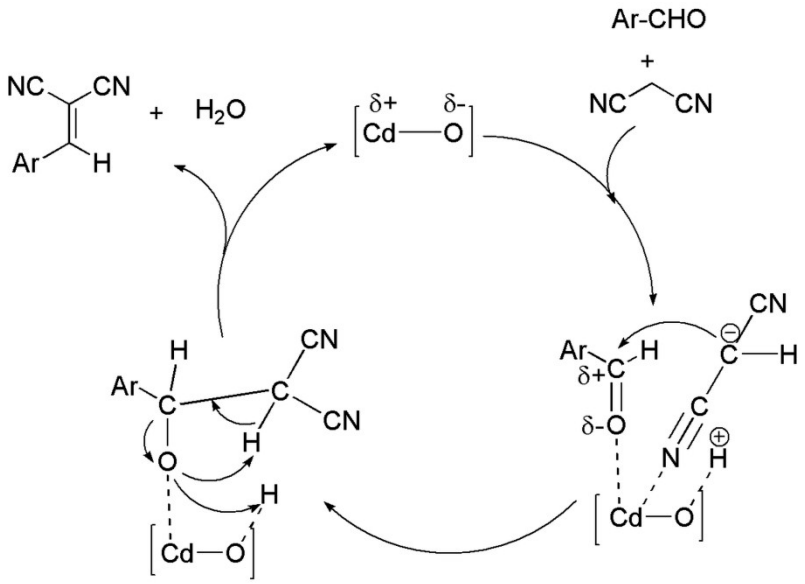
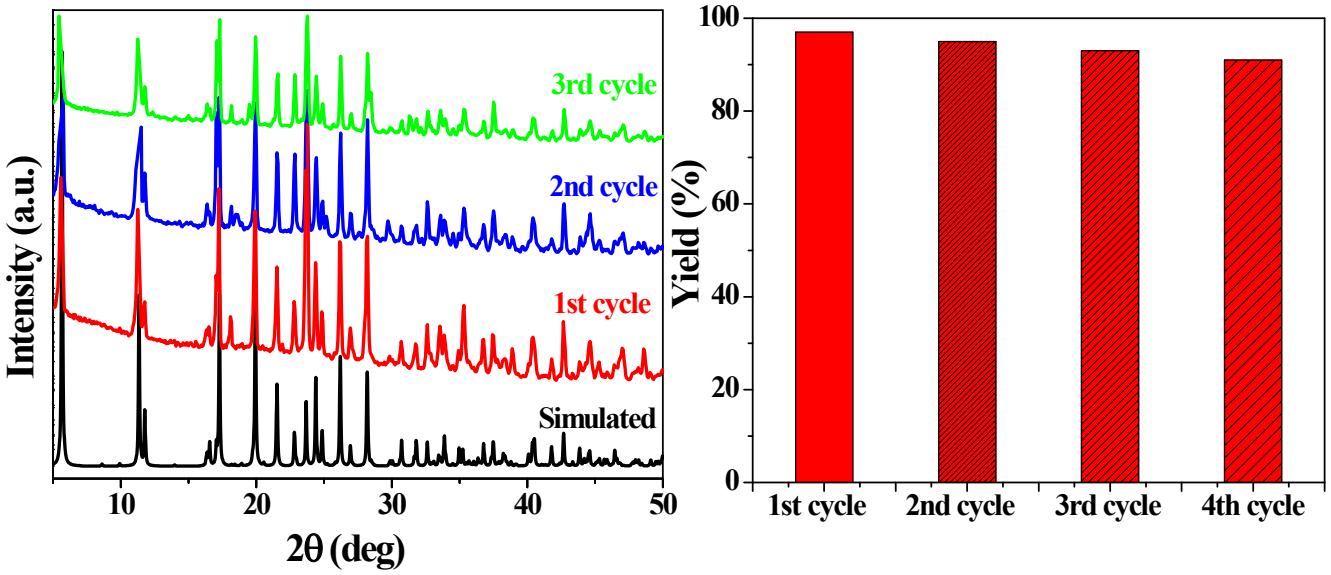


Fig. S17. The proposed mechanism of Knoevenagel condensation reaction.



(a) (b)

Fig. S18. (a) The pxrd patterns after the several cycles of Knoevenagel condensation reaction employing compound **1** as a catalyst. (b) The yield for recyclability test up to 4th cycles using compound **1** as a catalyst.

2-Benzylidenemalononitrile

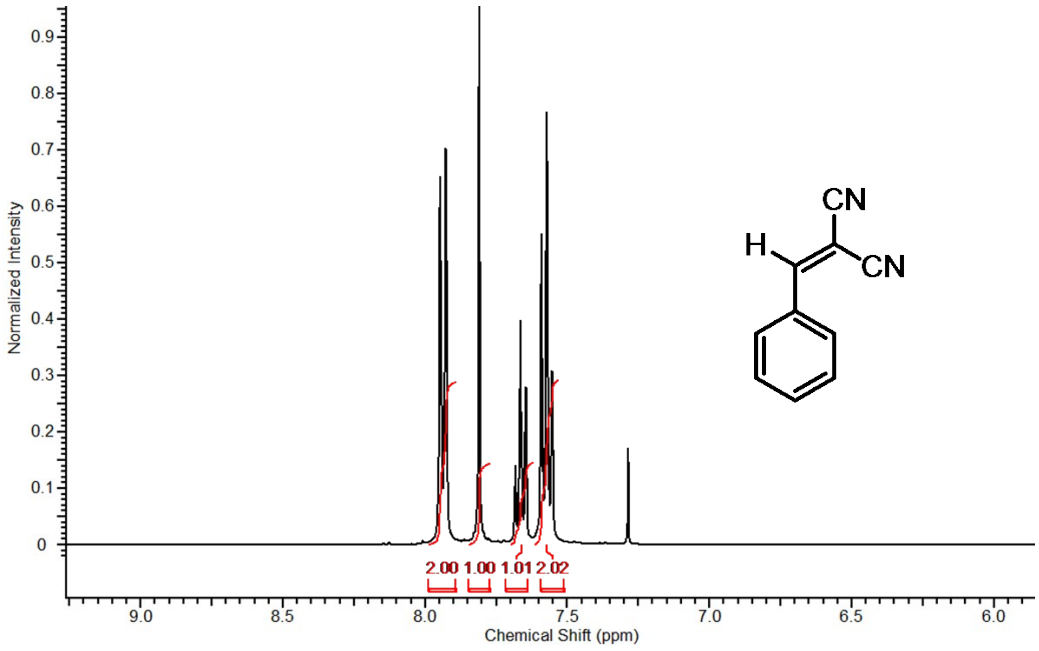


Fig. S19. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (t, 2H, J = 8.0 Hz, 8.0 Hz), 7.66 (t, 1H, J = 8.0 Hz, 8.0 Hz), 7.81 (s, 1H), 7.93 (d, 2H, J = 8.0 Hz)

2-(2-Nitrobenzylidene)malononitrile

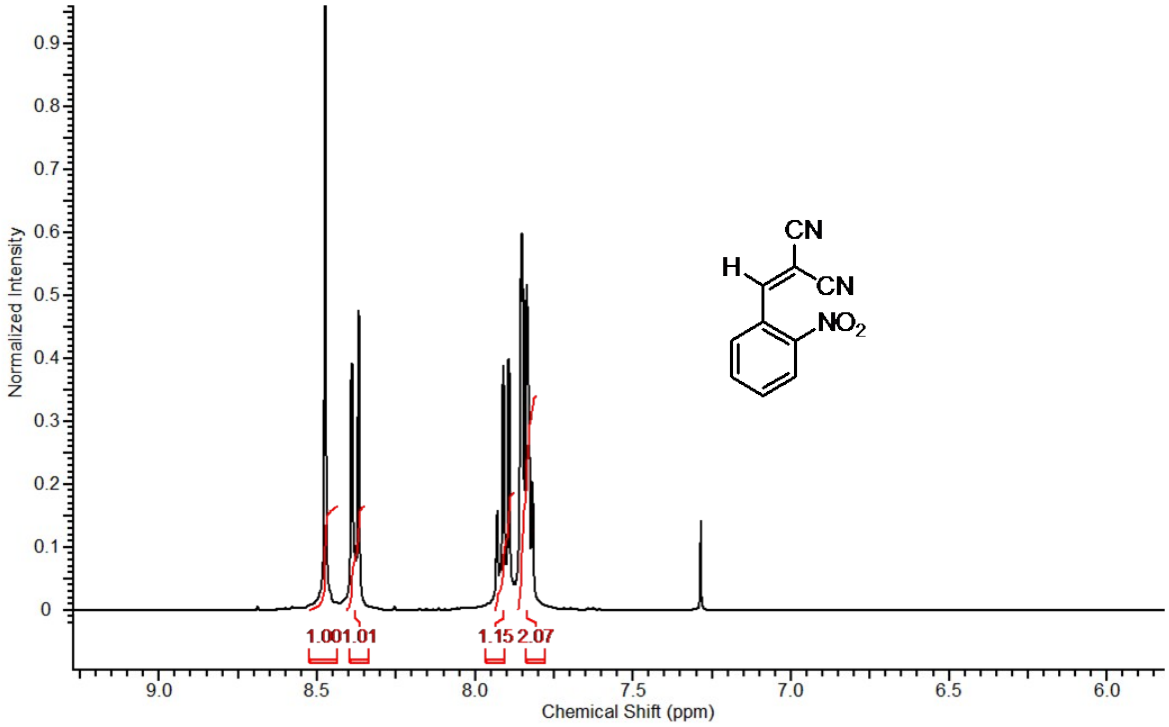


Fig. S20. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (m, 2H), 7.91 (t, 1H, J = 8.0 Hz, 8.0 Hz), 8.37 (d, 1H, J = 8.0 Hz), 8.47 (s, 1H).

3-(2,2-Dicyanovinyl)benzonitrile

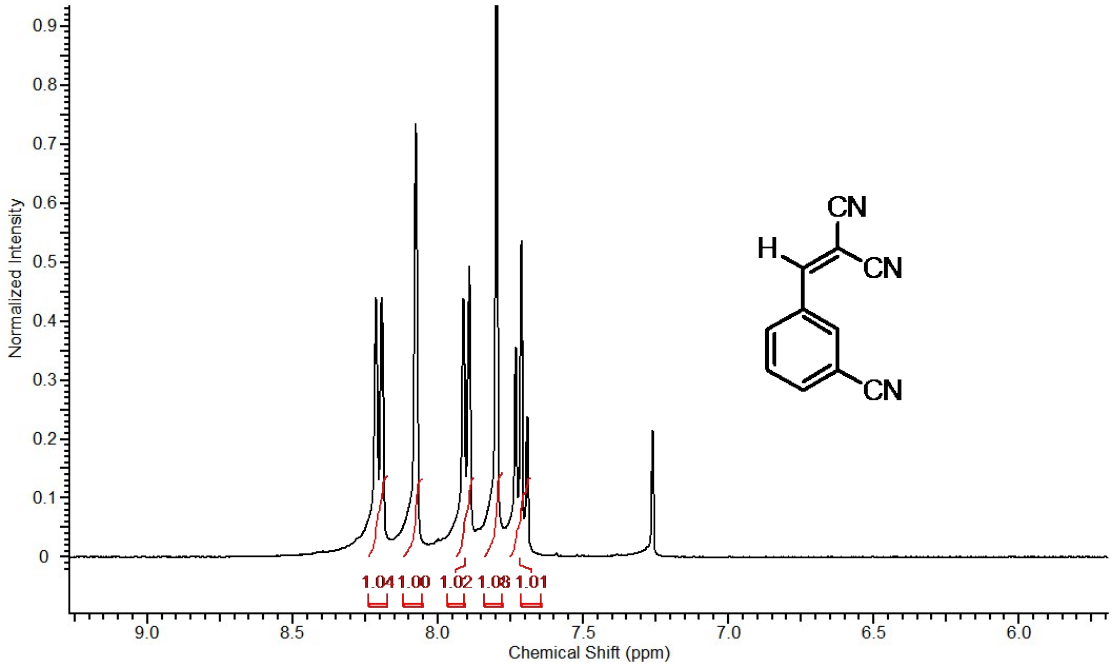


Fig. S21. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (t, 1H, J = 8.0 Hz, 8.0 Hz), 7.80 (s, 1H), 7.90 (d, 1H, J = 8.0 Hz), 8.08 (s, 1H), 8.20 (d, 1H, J = 8.0 Hz).

2-(4-Nitrobenzylidene)malononitrile

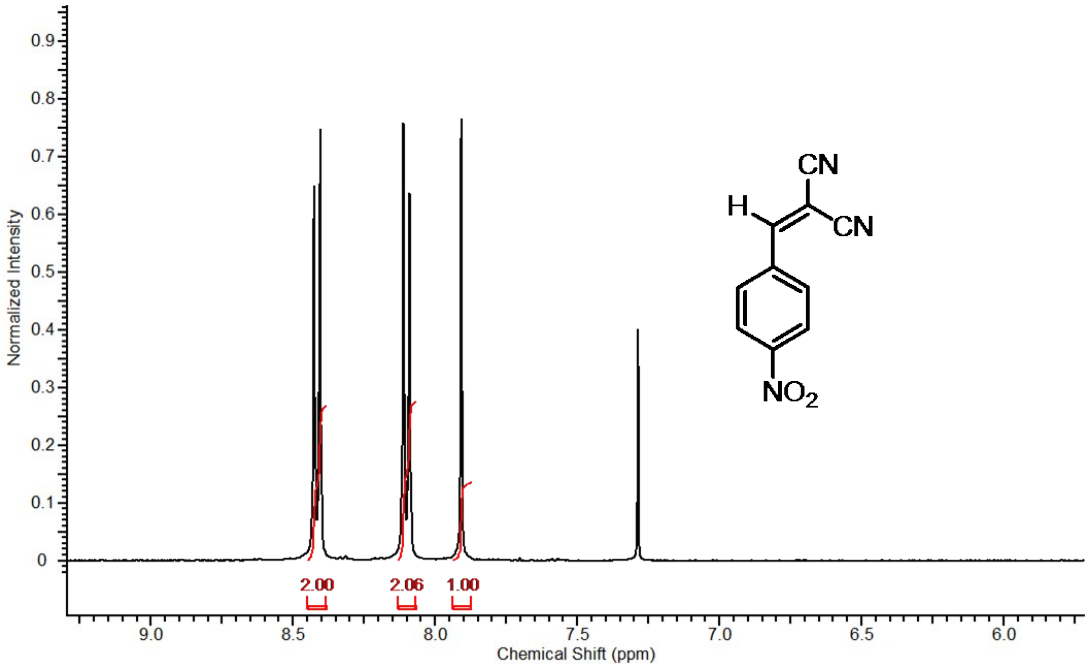


Fig. S22. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 1H), 8.10 (d, 2H, J = 8.0 Hz), 8.41 (d, 2H, J = 8.0 Hz).

2-(4-Chlorobenzylidene)malononitrile

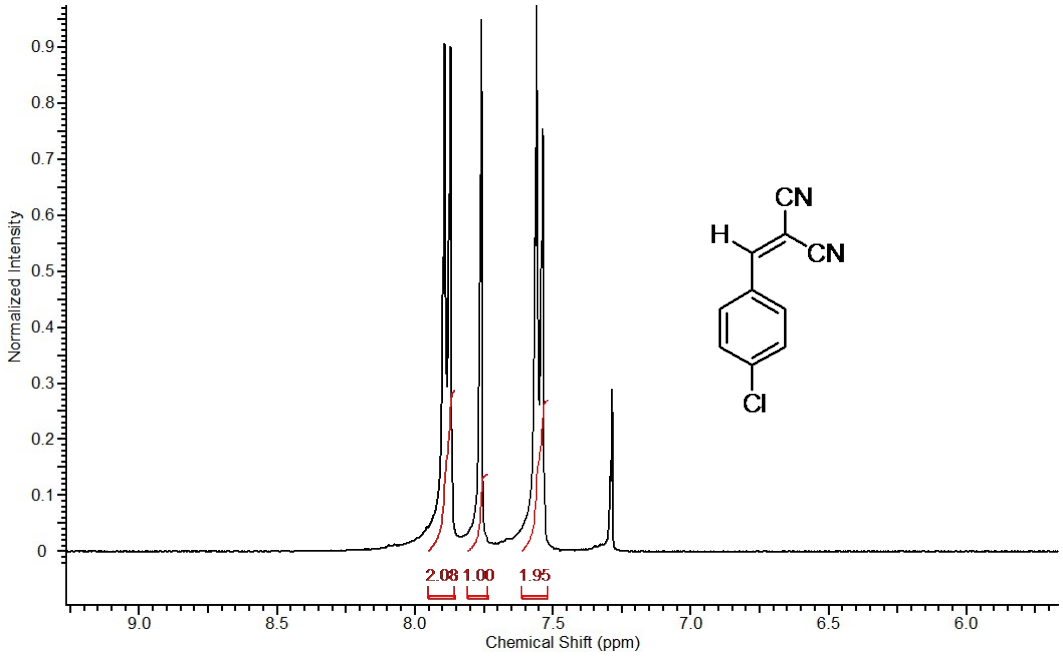


Fig. S23. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, 2H, J = 8.0 Hz), 7.76 (s, 1H), 7.88 (d, 2H, J = 8.0 Hz).

2-(4-Bromobenzylidene)malononitrile

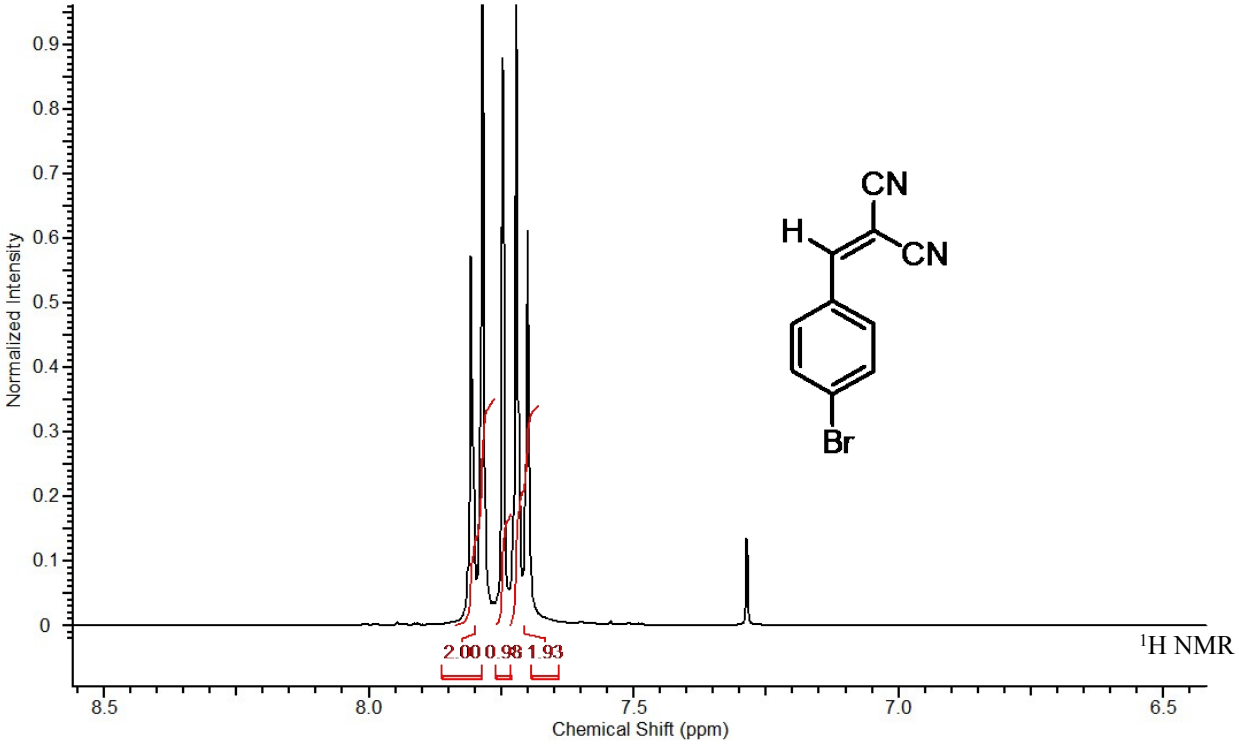


Fig. S24. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, 2H, J = 8.0 Hz), 7.75 (s, 1H), 7.80 (d, 2H, J = 8.0 Hz).