Supporting Information

Devising Mixed-Ligand Based Robust Cd(II)-Framework From Bi-Functional Ligand for Fast Responsive Luminescent Detection of Fe^{3+} and Cr(VI) Oxo-Anions in Water With High Selectivity and Recyclability

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Physical measurements

The infrared spectra (IR) of the samples were recorded using the KBr pellet method on a Perkin–Elmer GX FTIR spectrometer in the region of 400-4000 cm⁻¹. Powder X-ray diffraction (PXRD) data were collected using a PANalytical Empyrean (PIXcel 3D detector) System equipped with Cu Kα (λ=1.54 Å) radiation. Microanalyses of the compounds were Conducted using elementary vario MICRO CUBE analyser. Thermogravimetric analyses (TGA) (heating rate of 5 °C/min under N₂ atmosphere) were performed with a Mettler Toledo Star SW 8.10 system. The solvent-exchanged (methanol-exchanged) frameworks were then degassed overnight under vacuum at 120 °C to generate 11a. UV-Vis spectra recorded using Shimadzu UV-3101 PC spectrometer and the luminescence experiments were performed at room temperature using a Fluorolog Horiba Jobin Yvon spectrophotometer.

Chemicals

Analytical grade cadmium nitrate hexahydrate Cd(NO₃)₂·4H₂O (AR) and 4,4’-bipyridine were purchased from Tokyo Chemical Industries private limited. All the solvents such as N, N'-dimethylformamide (DMF) (Fisher Scientific), methanol (S. D. Fine Chemicals, India), were purchased and used without any further purification. Ligand (1H-imidazol-1-yl)benzoic acid was synthesised as mentioned in SI. All the metals salts used for the sensing experiments were procured commercially and used with any further analysis.

Single Crystal X-ray Crystallography

Single crystals with suitable dimensions were chosen under an optical microscope and mounted on a glass fibre for data collection. Intensity data for as synthesized colorless crystals of CSMCRI-11 were collected using graphite-monochromated MoKα (λ=0.71073 Å) radiation on a Bruker SMART APEX diffractometer equipped with CCD area detector at 173 K, The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The data integration and reduction were performed with SAINT software. Absorption corrections to the collected reflections were accounted with SADABS using XPREP. The structure was solved by direct method using SIR-97 and was refined on F² by the full-matrix least-squares technique using the SHELXL-2014 program package. All H atoms were placed in calculated positions using idealized geometries (riding model) and assigned fixed isotropic displacement parameters using the SHELXL default. To give an account of disordered electron densities associated with solvent molecules, the “SQUEEZE” protocol in PLATON was applied that produced a set of solvent free diffraction intensities. Final cycles of least-squares refinements improved both the R values and Goodness of Fit with the modified data set after subtracting the contribution from the disordered solvent molecules, using SQUEEZE program. The crystal and refinement data for solvent free CSMCRI-11 is listed in Table S1.
Figure S1. (a) Asymmetric unit of CSMCRI-11 and (b) demonstration of \( \pi-\pi \) stacking interactions between the benzene rings of ligand in the structure.

Synthesis of ligand and CSMCRI-11

The ligand 4-(1H-imidazol-1-yl) benzoic acid was prepared by slight modification of the following known procedure.\(^1\)

\[
\begin{align*}
\text{F} & \quad \text{DMF} \quad \text{K}_2\text{CO}_3 \\
\text{CN} & \quad \text{imidazole} \\
\end{align*}
\]

**Scheme S1.** Synthetic scheme of ligand.

In a round bottom flask 8g of K\(_2\)CO\(_3\) (activated), 2.1g of imidazole and 3.63g of 4-fluorobenzonitrile were dissolved in anhydrous DMF. Solution was stirred under N\(_2\) atmosphere and heated at 130 °C for 24 h. Afterwards, mixture was poured in ice cold water and allowed to stand for 24 h. The white ppt were filtered and was dissolved in ethanol (50ml) followed by dropwise addition of 6 N KOH solution (50 ml) and it was refluxed at 80 °C for 12 hours.

Reaction was cooled and resulting solution was acidified (pH 4.0) by 3 N HCl under ice-cold condition, which yields white precipitate. This was separated by filtration and washed several times with water. Finally, the white crude solid was dried at room temperature, followed by overnight vacuum drying. Ligand was characterised by LCMS (fig. 1a) and NMR (fig. 1b).
Figure S2. (a) ESI-MS spectrum of 4-(1H-imidazol-1-yl) benzoic acid (HL), (b) $^1$H-NMR spectrum of -(1H-imidazol-1-yl) benzoic acid (HL).
Scheme S2. Synthetic scheme of the MOF [Cd$_{1.5}$(L)$_2$(bpy)(NO$_3$)].DMF·2H$_2$O (CSMCRI-11).

Figure S3. SEM images of as-synthesised CSMCRI-11.

Figure S4. FT-IR spectra (KBr pellets, cm$^{-1}$) of CSMCRI-11 (black) and 11a (red).
Figure S5. Thermogravimetric analysis of as-made CSMCRI-11 (a) and 11a (b).

Figure S6. PXRD pattern of 11a after exposure to water for 10 days.
Figure S7. (a) UV-Vis spectra of constituting ligands of CSMCRI-11, and 11a (b) Emission intensity of ligand HL, bpy linker, and 11a (all dispersed in H2O). (c) Emission intensity of 11a dispersed in various solvents. (d) Emission spectra of 11a in water dispersion and supernatant solution after removal of 11a (red line). (e) UV-Vis spectra of 11a in different solvents.
Figure S8. Fluorescence quenching efficiency of 11a (1 mg/50 mL water) for different Cations. Quenching efficiency is calculated using equation \((I_0 - I)/I_0 \times 100\%\), where \(I\) and \(I_0\) denotes the emission intensities after and before the addition of studied analytes, respectively.

Figure S9. Linear region of fluorescence intensity of 11a upon addition of Fe\(^{3+}\) (0 – 120 μM)
Figure S10. Fluorescence quenching efficiency of 11a (1 mg/ 50 mL water) for different Anions. Quenching efficiency of 11a is calculated using equation \( \frac{I_0 - I}{I_0} \times 100\% \), where \( I \) and \( I_0 \) denotes the emission intensities after and before the addition of studied analytes, respectively.

Figure S11. Linear region of fluorescence intensity of 11a upon addition of \( \text{Cr}_2\text{O}_7^{2-} \) (0 – 120 \( \mu \)L, 10 \( \mu \)M stock solution).
Figure S12. Linear region of fluorescence intensity of 11a upon addition of CrO$_4^{2-}$ (0 – 120 μL, 10 μM stock solution).

Figure S13. PXRD curves of 11a after five sensing recovery cycles for Fe$^{3+}$, Cr$_2$O$_7^{2-}$, CrO$_4^{2-}$ (2.5 mM), showing that structural integrity of the framework is maintained.
**Figure S14.** FTIR spectra of 11a, Fe$^{3+}$@11a, CrO$_4^{2-}$@11a, Cr$_2$O$_7^{2-}$@11a.

**Figure S15.** Spectral overlap between absorbance spectra of (a) cations (b) anions and absorption spectra/emission spectra of 11a in water.
Figure S16. Change in UV pattern upon adsorption of (a) Fe$^{3+}$ (b) CrO$_4^{2-}$ (c) Cr$_2$O$_7^{2-}$ up to 120 minutes.

Table S1. Crystal data and structure refinement for CSMCRI-11

| Identification code | CSMCRI-11 |
|---------------------|-----------|
| Empirical formula   | C$_{30}$H$_{22}$Cd$_{1.5}$N$_7$O$_7$ |
| Formula weight      | 761.17    |
| Temperature/K       | 273.15    |
| Crystal system      | monoclinic |
| Space group         | C2/c      |
| a/Å                 | 41.129(8) |
| b/Å                 | 11.649(2) |
| c/Å                 | 16.487(3) |
| α/°                 | 90        |
| β/°                 | 100.533(7)|
| γ/°                 | 90        |
| Volume/Å$^3$        | 7766(2)   |
| Z                   | 4         |
| $\rho$calc /g/cm$^3$| 0.651     |
| μ/mm$^{-1}$         | 0.437     |
| F(000)              | 3023.7    |
| Crystal size/mm$^3$ | 0.18 x 0.16 x 0.14 |
| Radiation           | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection /° | 4.02 to 56.88 |
| Index ranges        | -55 ≤ h ≤ 54, -15 ≤ k ≤ 15, -22 ≤ l ≤ 22 |
| Reflections collected | 52513   |
| Independent reflections | 9692 [R$_{int}$ = 0.0853, R$_{sigma}$ = 0.0724] |
| Data/restraints/parameters | 9692/0/408 |
| Goodness-of-fit on F$^2$ | 1.008   |
| Final R indexes [I>2σ (I)] | $R_1 = 0.0706$, w$R_2 = 0.1287$ |
| Final R indexes [all data] | $R_1 = 0.0912$, w$R_2 = 0.1377$ |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.39/-1.33 |
ICP analysis results and analysis:

10 mg of 11a was centrifuge after sensing experiment and supernated was collected and heated till dryness. Solid was again dissolved in freshly prepared aqua regia (3:1 (v/v) conc. HCl: HNO₃) (4 mL) and heated to 140 °C till dryness. Same process was repeated thrice to ensure complete digestion. Residues were solubilized in 10 ml H₂O and the obtained solutions were used for ICP analysis after required dilution. No trace of leached cadmium was observed and ICP results before and after sensing were found to be same confirming no encapsulation of the ions inside the framework.

Table S2. ICP analysis results for samples

| Entry | Sample Code     | After Analysis | Ratio (Cd:Others) |
|-------|-----------------|----------------|-------------------|
|       |                 | Cd  | Others  |                  |
| 1.    | Fe³⁺@11a       | 2.08| 0.31    | 6.7:1             |
| 2.    | Cr₂O₇²⁻@11a    | 1.92| 0.33    | 5.8:1             |
| 3.    | CrO₄²⁻@11a     | 2.14| 0.35    | 6.11:1            |
| 4.    | Superannuate Solution | 0.0 | --      | 00                |

Table S3. Calculation of standard deviation of fluorescence intensity and limit of Detection for 11a towards Fe³⁺

| Blank Reading (11a) | Fluorescence Intensity (CPS) |
|---------------------|------------------------------|
| Reading 1           | 540677                       |
| Reading 2           | 460677                       |
| Reading 3           | 470677                       |
| Reading 4           | 466594                       |
| Reading 5           | 588271                       |

Standard Deviation(σ)  56621.12305

The slope of the graph(K)  777033 µM⁻¹

Detection Limit(3σ/K)  0.219 µM

Limit of detection (Fe³⁺)  0.166 ppm

Limit of detection (Fe³⁺)  166 ppb
Table S4. Calculation of standard deviation of fluorescence intensity and limit of detection for 11a towards Cr$_2$O$_7^{2-}$

| Blank Reading (11a) | Fluorescence Intensity (CPS) |
|---------------------|------------------------------|
| Reading 1           | 540677                       |
| Reading 2           | 460677                       |
| Reading 3           | 470677                       |
| Reading 4           | 466594                       |
| Reading 5           | 588271                       |
| Standard Deviation(σ) | 56621.12305                  |
| The slop of the graph(K) | 1133280 µM$^{-1}$           |
| Detection Limit(3σ/K) | 0.150 µM                   |
| Limit of detection (Cr$_2$O$_7^{2-}$) | 0.114 ppm             |
| Limit of detection (Cr$_2$O$_7^{2-}$) | 114 ppb                 |

Table S5. Calculation of standard deviation of fluorescence intensity and limit of detection for 11a towards CrO$_4^{2-}$

| Blank Reading (11a) | Fluorescence Intensity (CPS) |
|---------------------|------------------------------|
| Reading 1           | 540677                       |
| Reading 2           | 460677                       |
| Reading 3           | 470677                       |
| Reading 4           | 466594                       |
| Reading 5           | 588271                       |
| Standard Deviation(σ) | 56621.12305                  |
| The slop of the graph(K) | 718695 µM$^{-1}$           |
| Detection Limit(3σ/K) | 0.236 µM                   |
| Limit of detection (CrO$_4^{2-}$) | 0.179 ppm             |
| Limit of detection (CrO$_4^{2-}$) | 179 ppb                 |
Table S6. A comparison of quenching constants and corresponding LODs for various luminescent MOFs used for detection of Fe³⁺.

| Entry | Fluorescence Material | Medium        | \(K_\text{q} \text{ (M}^{-1}\text{)}\) | Detection Limit | Reference                          |
|-------|-----------------------|---------------|---------------------------------------|-----------------|------------------------------------|
| 1     | \{Eu\(_2\)(L\(_2\))\(_2\)\(_2\)(HCOO)\(_2\)(H\(_2\)O)\(_6\)\} \(_n\) | DMF           | 1.58×10\(^3\)                        | 3.3 × 10\(^{-3}\) M | Dalton Trans. 2013, 42, 12403-12409 |
| 2     | Eu(L\(_2\))\(_3\)     | Water         | 4.1 × 10\(^{3}\)                     | 5 × 10\(^{-4}\) M | ACS Appl. Mater. Interfaces 2013, 5, 1078-1083 |
| 3     | [Ni(L\(_3\))\(_2\)((H\(_2\)O)\(_2\))] | DMF           | 4.8×10\(^{-5}\)                      | Inorg. Chem. 2017, 56, 2936-2940 |
| 4     | [Cd\(_2\)(L\(_2\))(H\(_2\)O)] | DMF           | 3.6×10\(^{-5}\)                      | Inorg. Chem. 2016, 55, 3952-3959 |
| 5     | [Eu(L\(_2\))\(_2\)(NO\(_3\))]\(_2\)H\(_2\)O \(_n\) | ethanol       | 2.6×10\(^{-5}\)                      | Inorg. Chem. 2016, 55, 10114-10117 |
| 6     | [Eu(Hpzbc)\(_2\)(NO\(_3\))]\(_2\)H\(_2\)O \(_n\) | Ethanol       | 2.6×10\(^{-5}\)                      | Inorg. Chem. 2016, 55, 3952-3959 |
| 7     | \{Cd(5-asba)(binb)\}\(_n\) | Water         | 1.78×10\(^{4}\)                      | J. Mater. Chem. C 2016, 4, 11404-11418 |
| 8     | [Tb\(_3\)(TCA)\(_3\)(DMA)\(_2\)(OH)\(_2\)\(_3\)(H\(_2\)O)\(_2\)] | Water/Methanol | 3.71×10\(^{4}\)                     | 8 × 10\(^{-6}\) M | RSC Adv. 2016, 6, 94622-94628 |
| 9     | \{Cd(L\(_3\))(BPDC)\}\(_2\)H\(_2\)O \(_n\) | Water         | 3.63×10\(^{4}\)                      | Cryst. Growth Des. 2017, 17, 67-72 |
| 10    | \{Cd(L\(_3\))(L\(_3\))\}\(_2\)H\(_2\)O \(_n\) | DMF           | 5.57×10\(^{4}\)                      | 2.5×10\(^{-6}\) M | Dalton Trans. 2017, 46, 2332-2338 |
| 11    | 534-MOF-Tb(L\(_2\))\(_3\) | Water         | 5.51×10\(^{3}\)                      | 0.13 mM          | J. Mater. Chem. C 2017, 5, 2015-2021 |
| 12    | [Eu(HL\(_1\))(DMF)(H\(_2\)O)\(_2\)] | Ethanol       | 1519                                 |                 | Chem. Eur. J. 2015, 21, 15806-15819 |
| 13    | Al-MIL-53-N\(_3\) | Ethanol       | 6.13×10\(^{3}\)                      | 3×10\(^{-8}\) M  | Dalton Trans. 2018, 47, 2690–2700 |
| 14    | BUT-15                  | Ethanol       | 1.66×10\(^{4}\)                      | 3×10\(^{-7}\) M  | ACS Appl. Mater. Interfaces 2017, 9, 10286-10295 |
| 15    | \{Eu(Pyridine-Carboxylate)\(_2\)(BPDC)\(_2\)(NO\(_3\))\(_2\)::\(_2\)H\(_2\)O \(_n\) | DMF           | 5.16×10\(^{4}\)                      |                 | ACS Appl. Mater. Interfaces 2017, 9, 1629-1634 |
| 16    | Cd\(_3\)(bptc)(2,2’-bipy)\(_2\)(H\(_2\)O)\(_2\) | Ethanol       | 1.9×10\(^{4}\)                      | 1.02×10\(^{-4}\) M | Inorg. Chem. 2017, 56, 11768-11778 |
| 17    | La(TPT)(DMSO)\(_2\) | Ethanol       | 1.36 × 10\(^{4}\)                    |                 | Dalton Trans. 2015, 44, 13340-13346 |
| 18    | [Zn\(_2\)(TPOM)(NDC)\(_2\)] | Ethanol       | 1.9×10\(^{4}\)                      | 2×10\(^{-6}\) M  | Inorg. Chem. 2017, 56, 12348-12356 |
| 19    | [Zn\(_2\)(OH)\(_2\)(C\(_5\)H\(_4\)O\(_2\)S\(_2\)\(_2\)]\(_2\)\(_2\)5DMF\(_\_\)\(_2\)\(_2\)H\(_2\)O | Ethanol       | 9.1×10\(^{3}\)                      | 1.8×10\(^{-4}\) M | Dalton Trans. 2018, 47, 1159–117 |
| 20    | [Cu\(_2\)(L\(_2\))\(_2\)(BDC)\(_2\)] | DMF           | 1.67×10\(^{4}\)                      | 162ppb          | J. Mater. Chem. A 2017, 5, 15797–15807 |
| 21    | [Zn\(_3\)(L\(_2\))\(_2\)(bipy)](µ\(^3\)-OH)\(_2\))(H\(_2\)O) | Ethanol       | 2.3×10\(^{4}\)                      | NA              | Sensors and Actuators B 2018, 257, 207–213 |
| 22    | [Tb\(_2\)(TDC)(CH\(_3\)OH)\(_2\)](CH\(_3\)OH) | Ethanol       | 9.52×10\(^{3}\)                      | NA              | RSC Adv. 2016, 6, 91741–91747 |
| 23    | Eu\(_3\)(MFDA)\(_2\)(HCOO)\(_2\)(H\(_2\)O)\(_6\) | DMF           | 1.58×10\(^{3}\)                      | 0.3µM           | Dalton Trans. 2013, 42, |
L₁ = 9,9-dimethylfluorene-2,7-dicarboxylic acid, L₂ = 4’-(4-carboxyphenyl)-2,2’:6’,2’-terpyridine, L₃ = 4,4’-oxidibenzoic acid, L₄ = 3,5-bis{(pyridin-4-y1)thiophen-2-yl}pyridine, L₅ = 3-(1H-pyrazol-3-yl) benzoic acid, L₆ = 4,4’,4’-s-triazine-1,3,5-triyltri-m-aminobenzoate, L₇ = 4,4’-(2,5-bis(methythio)-1,4-phenylene)dipyridine, L₈ = 5,8-di(1H-imidazol-1-yl)quinoxaline, L₉ = 5-hydroxyisophthalic acid, L₁₀ = 2,4,6-tris[(3-carboxylphenoxy) ylmethyl]mesitylene, L₁₁ = 2,8,14,20-tetra-ethyl-6,12,18,24-tetra-methoxy-4,10,16,22-tetra-carboxy-methoxy-calix[4]arene, (H₃TPT) = p-terphenyl-3,4‴,5-tricarboxylic acid

**Table S7.** A comparison of quenching constants and corresponding LODs for various luminescent MOFs used for detection of Cr₂O₇²⁻/CrO₄²⁻:

| Entry | Material | Analyte | Solution | Ksv (M⁻¹) | Detection Limit (M) | Reference |
|-------|----------|---------|----------|-----------|---------------------|-----------|
| 1     | [Zn(L₁)(L₂)]ₙ | Cr₂O₇²⁻/CrO₄²⁻ | H₂O      | 1.37×10³ / 1.00×10³ | 1.20×10⁻⁵ / 1.83×10⁻⁵ | Inorg. Chem. 2017, 56, 2627-2638 |
|       | [Cd(L₁)(L₂)]ₙ | Cr₂O₇²⁻/CrO₄²⁻ | H₂O      | 2.91×10³ / 1.30×10³ | 2.26×10⁻⁶ / 2.52×10⁻⁶ | J. Mater. Chem. A 2016, 4, 15494-15500 |
| 2     | [Zn₂(L₃)(L₄)₂]·4H₂O | Cr₂O₇²⁻/CrO₄²⁻ | DMF      | 7.59×10³ / 4.45×10³ | 3.9×10⁻⁶ / 4.8×10⁻⁶ | New J. Chem. 2016, 40, 610 4654-4661 |
| 3     | Eu³⁺ @ MIL-121 | Cr₂O₇²⁻ |          | 4.34×10³ | 0.054 µM | Inorg. Chem. 2016, 55, 3952-3959 |
| 4     | [Eu(L₅)(NO₃)]·H₂O | Cr₂O₇²⁻ | ethanol  |          | 2.2×10⁻⁵ | Cryst. Growth Des. 2017, 17, 67-72 |
|       | [[Cd(L₆)(L₇)]·2H₂O]ₙ | Cr₂O₇²⁻ | H₂O      | 6.4×10³ | 3.76×10⁻⁵ | Inorg. Chem. 2017, 56, 4197-4205 |
|       | [[Cd(L₆)(L₇)]·H₂O·0.5H₂O]ₙ | Cr₂O₇²⁻ | H₂O      | 4.97×10³ | 4.86×10⁻⁵ | Inorg. Chem. 2017, 56, 4197-4205 |
| 5     | [Eu₂(L₆)₆CO₇·4H₂O]·DMF·solvent | Cr₂O₇²⁻/CrO₄²⁻ | H₂O      | 1.04×10⁴ / 4.85×10³ | 3.64×10⁻⁶ / 1.70×10⁻⁶ | CrystEngComm 2016, 18, 4445-4451 |
| 6     | [Zn(btz)]ₙ | Cr₂O₇²⁻/CrO₄²⁻ | H₂O      | 2.43×10³ / 3.19×10³ | 0.05 µM | Chem. Eur. J. 2015, 21, 11475-11482 |
|       | [Zn₂(ttz)H₂O]ₙ | Cr₂O₇²⁻/CrO₄²⁻ | H₂O      | 2.19×10³ / 2.35×10³ | 0.05 µM | Inorg. Chem. 2017, 56, 14178-14188 |
| 7     | [Cd₃(L₁₀)(bib)(DMF)₃] | Cr₂O₇²⁻/CrO₄²⁻ | H₂O      |          |          | Inorg. Chem. 2017, 56, 14178-14188 |
| 8     | NU-1000 | Cr₂O₇²⁻ | H₂O      | 1.33×10⁴ | 1.8 µM | Inorg. Chem. 2017, 56, 14178-14188 |
| 9     | [Ni₂(μ₂-OH)(azdc)(tpim)][NO₃]·6DMA·6MeOH | Cr₂O₇²⁻/CrO₄²⁻ | H₂O      | 7.90×10³ / 1.31×10⁴ | 0.9 / 0.29 ppm | ACS Appl. Mater. Interfaces 2019, 11, 43, 40134-40150 |
| 10    | [Y(BTC)(H₂O)₆]₀.1Eu | Cr₂O₇²⁻/CrO₄²⁻ | H₂O      | 1.18×10⁷ / 4.52×10³ | 0.03 / 0.04 µM | Microporous Mesoporous |
$L_1$=isophthalic acid (H$_2$IPA) and $L_2$=3-pyridylcarboxaldehyde nicotinoylhydrazone $L_3$(TPOM) = tetrakis(4-pyridyloxymethylene)methane $L_4$(NH$_2$–BDC) = 2-aminoterephthalic acid), $L_5$(H$_2$pzbc) = 3-(1H-pyrazol-3-yl) benzoic acid) $L_6$ = 4,4’-(2,5-bis(methylthio)-1,4-phenylene)dipyridine, $L_7$ = 4,4’-biphenyldicarboxylic acid, $L_8$ = 4,4’-sulfonyldibenzonic acid, $L_9$ (Htpbpc) = 4’-[4,2’;6’,4”]-terpyridin-4’-yl-biphenyl-4-carboxylic acid, $L_{10}$= hexa[4-(carboxyphenyl)oxamethyl]-3-oxapentane acid

Reference:

1Nandi, S., Haldar, S., Chakraborty, D., & Vaidhyanathan, R. (2017). Strategically designed azolyl-carboxylate MOFs for potential humid CO$_2$ capture. *Journal of Materials Chemistry A*, 5(2), 535-543.