

Isolation and Characterization of Zn^{II} and Hg^{II} Coordination Polymers with a Designed Azo-Aromatic Ligand: Identification of Micrometer- and Nanometer-Sized Particles

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Controlled layering of the deprotonated methanolic solution of the azo-aromatic ligand [L³][−] (HL³ = 2-[3-(pyridylamino)-phenylazo]pyridine) over the aqueous/methanolic solutions of metal chlorides MCl₂ (M = Zn, Hg) afforded nano- and micrometer-sized particles of the metal–organic polymeric complexes of [HgCl(C₁₆H₁₂N₅)]_∞ (**1**) and [ZnCl(C₁₆H₁₈N₅O₃)]_∞ (**2**). Time-dependent growth of the above particles is followed by the SEM and TEM analyses of the samples at different time intervals. The X-ray structure of the mercury polymer reveals that two infinite 1D, *zigzag* chains composed of [HgCl(L³)]_∞ units run along the *a* axis antiparallelly. The polynuclear Zn compound, in contrast, agglomerates fast to form hemispherical microcrystals with a diamondoid surface morphology, and no suitable X-ray quality

crystal of this complex could be isolated. Powder XRD analyses of the samples as well as thermogravimetric analysis (TGA) are used for their characterization. Unusually, these metal–organic polymers of the reference d¹⁰ metal ions are green and absorb in the low-energy region of the visible spectrum, 660–675 nm. Semiempirical calculations on a representative complex **1** suggest that the transitions in the complexes involve ligand orbitals. These also show multiple emissions in the blue-green region. The Zn complex, which is microporous, shows reversible adsorption/desorption of N₂ and H₂ gasses. The mercury polymer, on the other hand, shows poor adsorption ability.

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Introduction

Inorganic as well as organic polymeric substances have attracted intensive attention during the recent years primarily because of their potential applications as functional materials.^[1] In the past decade, several organic and inorganic materials^[2] have been synthesized and investigated. In contrast, examples^[3,4] of nano- or micrometer-scale particles of metal–organic coordination polymers are limited. Thus, their preparation is challenging owing to their ability to tailor their physical and chemical properties through deliberate selection^[5] of metal and multifunctional ligands. Various types of bridging ligands^[6–8] have been used for the construction of coordination polymers. However, such examples containing azo-aromatic bridging ligands are un-

common primarily because of the lack of availability of suitable ligands.^[8] Azo-aromatic compounds, with the exception of their use in dyestuff industry, have extensively been studied in recent years owing to their novel optical^[9] and redox properties. Low-lying vacant π*(azo) orbitals in metal–azo-aromatic compounds are responsible for low-energy transitions and the colour of the compounds. During recent years we have been working on the coordination chemistry of a new class of azo-aromatic ligands [HL]. Three different ligands HL¹, HL² and HL³ have been isolated^[10–12] following regioselective *ortho* fusion of suitable aromatic amines. The deprotonated ligand [L¹][−] binds in a bischelating fashion to produce monometallic complexes, the other two ligands, [L²][−] and [L³][−], each containing an additional pyridyl donor, serve as bridges between two or more metal centres. Moreover, the coordination mode of the deprotonated ligand [L³][−] is different from that of its positional isomer [L²][−] and is found to be suitable^[13] for the construction of one-dimensional polymeric material,^[14,15] particularly with coordinately unsaturated metal ions.

The primary concern of this paper is to report our results on the isolation of one-dimensional Hg^{II} and Zn^{II} coordination polymers with the bridging ligand [L³][−]. Unusually, the polymeric d¹⁰ metal complexes are intensely coloured and absorb in the low-energy region of the visible spectrum.

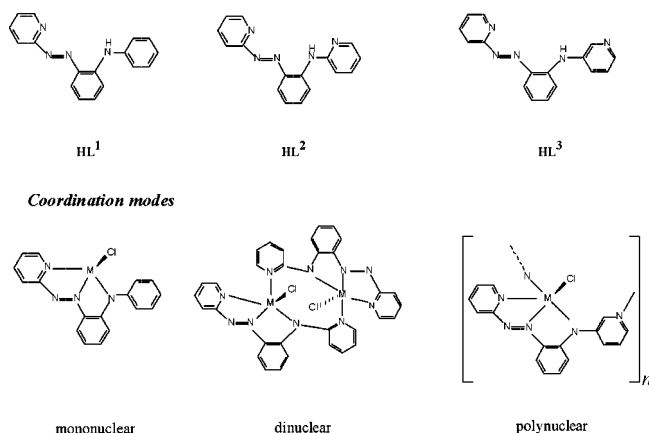
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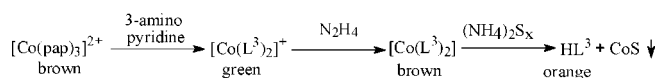
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These polymers form different-sized particles (micrometer to nanometer) at different time intervals under identical experimental conditions. Their growth processes have been followed by FESEM, TEM, HRTEM, XRPD, EDS and single-crystal X-ray data analysis of the frameworks.



Results and Discussion

The ligand HL³ has been synthesized by regioselective C–N bond fusion of 3-aminopyridine to cobalt(II)-coordinated 2-(phenylazo)pyridine following the reaction strategy developed by us^[10a] (Scheme 1).



Scheme 1.

The green cobalt complex [Co(L³)₂]ClO₄ was purified on a preparative TLC (silica gel) plate by using a chloroform/toluene (1:1) solvent mixture as eluent and was characterized spectroscopically. Its ¹H NMR spectrum is submitted as Figure S1 Supporting Information. Reduction of the cationic cobalt complex by dilute N₂H₄ followed by removal of [Co]²⁺ as CoS led to the isolation of the ligand [HL³] in moderate yield. The pure ligand was obtained as a yellow crystalline solid, whose ESI-MS spectrum shows an intense peak at *m/z* = 276 amu assigned to the [H₂L³]⁺ ion (Figure S2, Supporting Information). The ¹H and ¹³C NMR spectra of the ligand [HL³] (Figures S3 and S4, Supporting Information) corroborate fully with its formulation. The deprotonated ligand [L³][−] (generated in situ by addition of NEt₃) reacts spontaneously with the methanolic/aqueous solutions of MCl₂ (M = Zn, Hg) at room temperature. The dark green compounds, thus produced, are rapidly precipitated. However, by controlled layering of the deprotonated ligand solution over the solutions of metal salts, we could achieve the synthesis of stable particles of the reference metal–organic polymers. It may be noted here that the salt CdCl₂ failed to produce any stable compound under identical experimental conditions. Chemical compositions of the polymers were established on the basis of their elemental analyses. Both are pentacoordinate and have identical repeating units [MCl(L³)]. Notably, the morphology and the growth process of the mercury polymer are totally different from those of the zinc analogue. The growth processes of the two products are detailed separately.

Hg–L³ Polymer

For the evaluation of the crystalline mercury coordination polymer, the synthetic reactions were carried out in

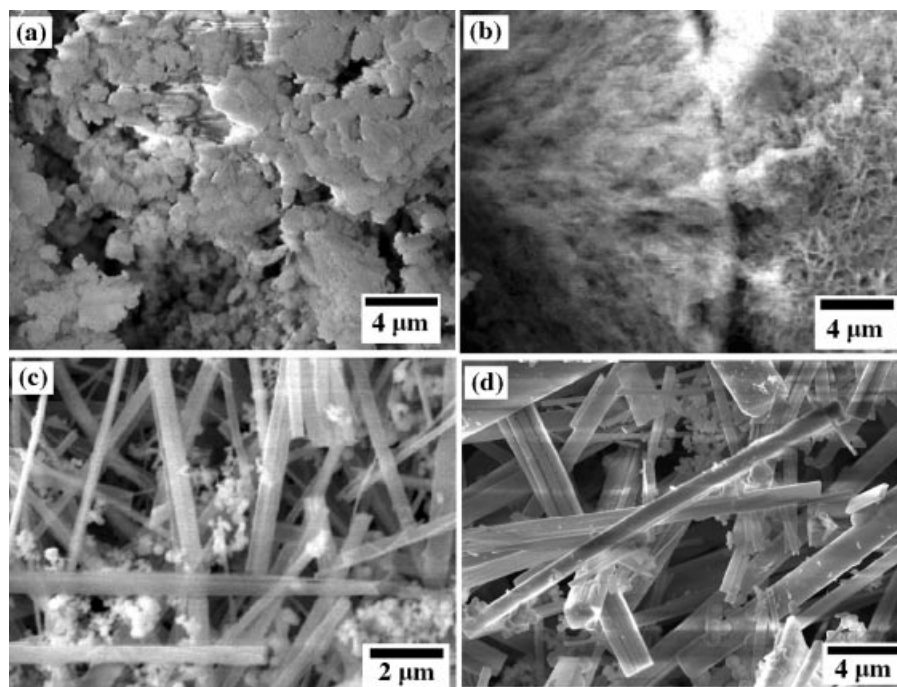


Figure 1. FESEM images of the [HgClL³]_∞ polymer at different time intervals: (a) 5 h, (b) 36 h, (c) 5 d, (d) 10 d.

five sealed glass tubes (A–E) under the same experimental conditions but with varying reaction times. A deprotonated methanolic solution of the ligand was layered over an aqueous solution of mercuric chloride and left undisturbed for diffusion (see Experimental Section). Figure 1a–d shows the SEM images of the as-synthesized products. It reveals the following features: (i) The product obtained from the tube A (after 5 h) is amorphous (Figure 1a); (ii) The SEM image (Figure 1b) of the second sample (tube B, after 36 h) reveals fine wirelike morphology; (iii) The SEM shown in Figure 1c is obtained from the third sample (tube C, after 5 d) and indicates the formation of nano-ribbonlike morphology. The width of these ribbons varies from a few nm to 500 nm, and their lengths lie within a few tens of micrometers. The facets of these ribbons are not well defined, which is an indication of their poor crystallinity; (iv) Interestingly, the fourth sample (tube D, after 10 d) is composed of well-defined microribbons (Figure 1d); and (v) X-ray-quality single crystals are obtained from tube E after 3 weeks and their X-ray structures are analyzed (*vide infra*).

For understanding the growth mechanism, we also investigated these samples by transmission electron microscopy (TEM). The first product is a featureless amorphous spherical compound, and the second is wirelike. The fourth sample (tube D) is quite thick for TEM measurement, and the electron beam failed to penetrate through it. Fairly interesting micrographs are obtained from the third sample (tube C). Figure 2a shows the TEM image of a single ribbonlike morphology. Closer observation of the image reveals the

presence of large quantities of spherical particles embedded within the structure. Figure 2b shows the magnified TEM image of a ribbon, which indicates the presence of a large number of dark, spherical nanoparticles. The TEM image in Figure 2d reveals the presence of a large number of spherical nanoparticles of the polynuclear mercury sample 1 with diameters that vary between 10 and 30 nm. Some grain agglomeration is also observed in this image and is indicated by arrows. It is also interesting to note, from the TEM images, the layered nature of the agglomerated particles, which can perhaps explain the reason for the rapid increase in the dimension of the products. Thus, on the basis of the SEM and TEM observations we can conclude that the crystalline metal–organic framework (MOF) is produced in four steps. The first step is the formation of amorphous nucleation centres, followed by formation of the one-dimensional amorphous framework; the amorphous nature is also evident from its featureless powder XRD pattern (Figure S5, samples of Figure 1a and b). The nanocrystalline particles act as the nucleation sites (thus formed within the amorphous network), absorb more reactants from the solution and agglomerate with each other to grow in one-dimension to form fine wire- or ribbonlike products. In the final step these products crystallize to yield large whiskerlike single crystals. This is as expected since the amorphous products are high-energy systems^[16] and have a natural tendency to minimize their energy by crystallization. Larger single-crystalline products are achieved if the reaction is allowed to take place for 3 weeks or more.

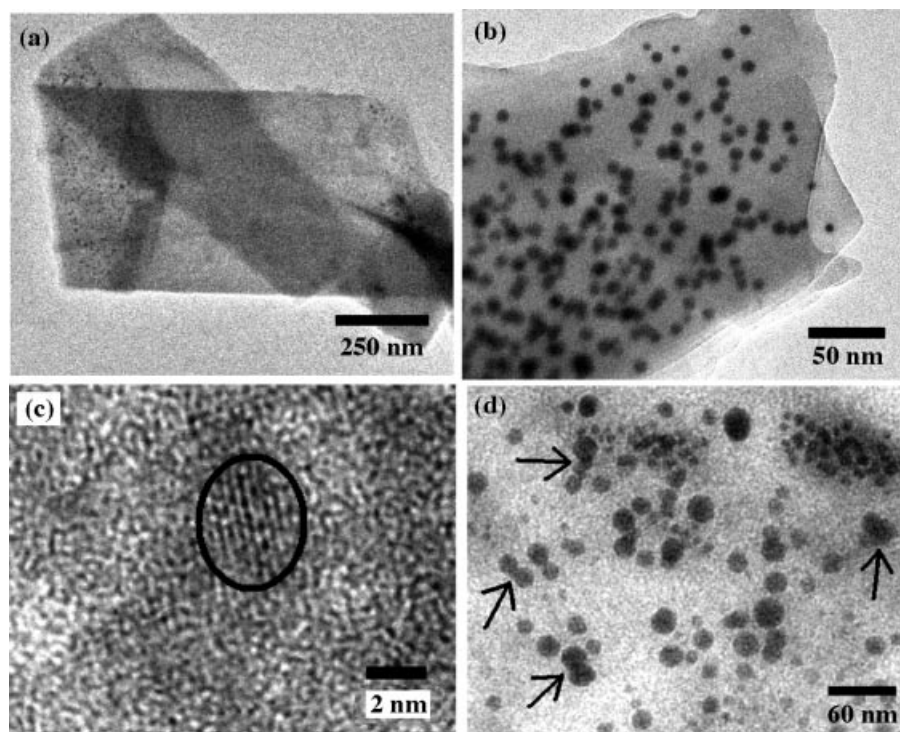


Figure 2. (a) TEM image of the single ribbonlike products of $[\text{HgCIL}_3]_\infty$. (b) Zoomed TEM image showing spherical nanoparticles of Hg containing MOF. (c) Representative zoomed HRTEM image of a single metal–ligand nanoparticle. (d) Arrows indicating the agglomeration of the particles.

We examined the XRPD pattern for all the samples obtained from the aforementioned five tubes (A–E). The sample from tube A exhibits a featureless XRPD pattern, which implies that it is amorphous. However, experimental XRPD patterns of the samples from the three tubes (B–D) are similar and consistent with the simulated pattern derived from the single-crystal (tube E). Thus, we conclude that the bulk sample has the same structure as that of the single crystal. The experimental powder diffraction pattern of a representative sample (tube C), along with the simulated pattern, are shown in Figure 3 for comparison. Furthermore, micro-elemental analyses of the above mercury samples reveal that they have an identical composition, $[\text{HgCl}(\text{L}^3)]$, which was further supported by energy dispersive spectroscopy (EDS) (Figures S6 and S7).

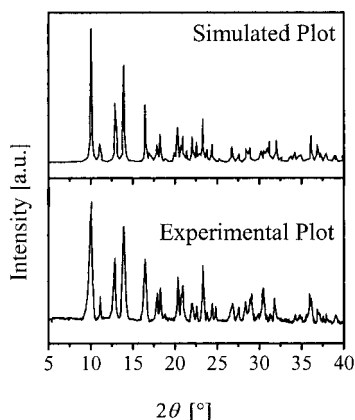


Figure 3. Experimental and simulated XRPD patterns of the as-synthesized mercury polymer $[\text{HgCl}(\text{L}^3)]_\infty$.

Zn– L^3 Polymer

The results obtained in this case were notably different from that of its mercury analogue. Here, two types of mi-

crometer-sized particles are identified. The SEM image of the products obtained after 1 d reaction time shows the formation of large numbers of nanorods bundled together (Figure 4a). With time, these particles grow in one direction, and the basal region crystals penetrate through each other and agglomerate to form large microcrystals. As these particles grow on the tube walls they cannot form spheres, instead hemispherical particles are isolated (Figure 4b). The SEM image of a hemispherical single unit (after 6 d) is shown in Figure 4c, and a further magnified image of it is displayed in Figure 4d. This reveals that the individual basic units with pyramidal tips interpenetrate^[16] to form the hemispherical particles. Figure 4e shows the broken basal region of a hemispherical crystal that indicates agglomeration^[17] of closely packed individual units. No suitable single crystal of this sample could be isolated in this case, possibly because of fast agglomeration, although the powder diffraction pattern indicates a crystalline nature (Figure 5). The Zn samples are too thick for TEM measurements; however, high resolution transmission electron microscopy

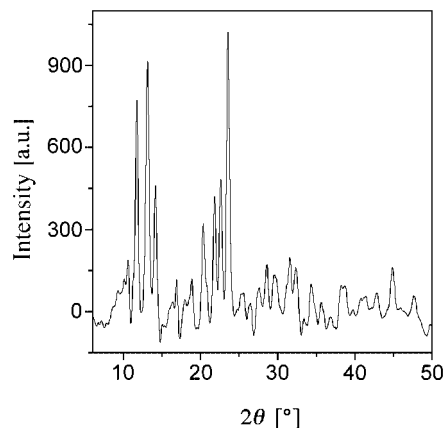


Figure 5. XRPD pattern of the polycrystalline polymer $[\text{ZnCl}(\text{L}^3 \cdot 3\text{H}_2\text{O})]_\infty$.

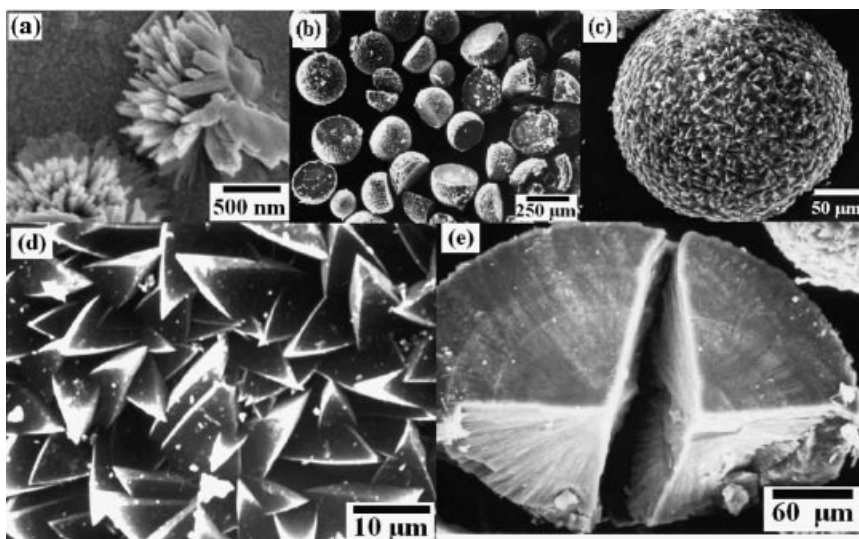


Figure 4. FESEM images of the $[\text{ZnCl}(\text{L}^3 \cdot 3\text{H}_2\text{O})]_\infty$ polymer at different time intervals: (a) 1 d, (b) 6 d, (c) Zoomed SEM image of one of the representative hemispheres, (d) Magnified surface image of (c), (e) Broken basal region of a hemisphere.

(HRTEM) on the crushed sample reveals that these particles are crystalline with a highly ordered arrangement of the micropores (Figure 6). Microelemental analyses on the Zn samples indicate that their compositions are similar to those of the mercury analogues, with the exception that the Zn polymer contains three H₂O molecules of crystallization per formula weight ([ZnCl(L³)]·3H₂O) of the repetitive building unit (TG analysis, vide infra). Energy dispersive spectra of these samples (Figures S8a and S8b) also corroborate the above formulation.

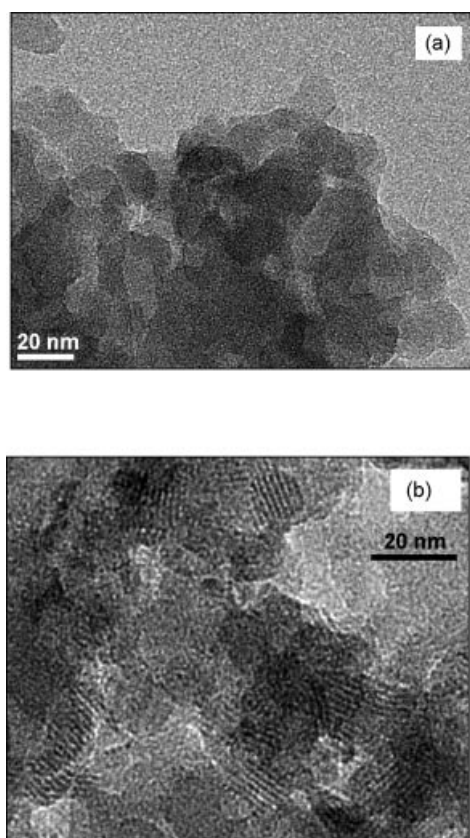


Figure 6. HRTEM images of the as-synthesized [ZnCl(L³·3H₂O)]_∞ polymer: (a) low magnification, (b) high magnification.

Crystal Structure of [HgCl(L³)]_∞ (1)

The three-dimensional structure of the mercury complex (sample obtained from tube E) was determined by single-crystal X-ray diffraction. In this structure, two 1D infinite polymeric chains made of [HgCl(L³)]_∞ units run antiparallelly along the *a* axis.^[18] As shown in Figure 7, each mercury atom in this molecule is in a pentacoordinated N₄Cl environment, and the geometry around each Hg^{II} ion may be described as distorted square pyramidal^[19] with a τ value of 0.21. In this context, we note that higher-coordination-number (>4) complexes of divalent mercury^[20] are scarce in the literature. In the molecule **1**, Hg(1) sits above the plane formed by the three coordinating nitrogen atoms, N(1), N(3) and N(4), by 0.0464(1) Å; this pattern is repeated throughout the polymeric chain. The bending of the

ligand and its coordination at the Hg centre result in *zigzag* chains that adopt a saw-tooth-like structure (Figure 8a). The two independent polymeric chains are closely packed/locked through metal- π interactions^[21a] along with face-to-face π - π ring interactions.^[21b] Notably, the metal- π interactions predominate over the π - π interactions. For example, the perpendicular distance between the centroids of the two interacting polymeric chains lies between 3.44 and 3.45 Å, whereas the distance between the Hg metal and centroid (Cg) lies in the range 3.37–3.41 Å. Selected bond lengths and angles, and the crystallographic data for the crystal [HgCl(L³)]_∞ are collected in Table 1 and Table 2, respectively. The secondary interactions in this structure (Figure 8b) work together to bring the two consecutive chains close together (Table 3 and Table 4). Notably, the closest distances between the two mercury atoms (both inter- and intramolecular) are quite long: intramolecular Hg(1)···Hg(1a) and Hg(2)···Hg(2a) distances are 6.243 Å and 6.307 Å, respectively, which are appreciably longer than the sum of the van der Waals radii^[12c,22] between two consecutive mercury atoms (3.50 Å). The distance between two mercury atoms to complete one pitch [irrespective of Hg(1) or Hg(2)] is 10.145 Å. The Hg- π and π - π interactions are depicted in Figure 8b. For comparison, we wish to note that the ligand HL² reacts with HgCl₂ to produce the soluble dinuclear mercury(II) blue complex, in which the two [L²]⁻ ligands bridge the two mercury centres.^[12c]

Spectral Properties

Infrared spectra of the two polymeric complexes [MCIL³]_∞ (M = Hg, Zn) are almost identical, and $\tilde{\nu}_{C=N}$ and $\tilde{\nu}_{N=N}$ appear^[12] in the range 1585–1600 cm⁻¹ and 1305–1325 cm⁻¹, respectively. These complexes also show characteristic $\tilde{\nu}_{M-Cl}$ bands that appear^[12] near 275 cm⁻¹. Both complexes are insoluble in common organic solvents, and their UV/Vis spectra in the solid state were studied. The lowest-energy transition in free [L³]⁻ (460 nm) is redshifted considerably by ca. 200 nm in the corresponding metal complexes. Whereas the mercury complex shows a broad transition at 660 nm, its zinc analogue absorbs at 675 nm. Notably, examples of d¹⁰ metal ion complexes that absorb in such a low-energy part of the visible region are uncommon.^[12] In order to gain some insight into the nature of the orbitals involved in electronic transitions of the above complexes, semiempirical EHMO calculations on the representative mercury complex [HgCIL³]_∞ was performed with the program CACAO^[23] created by Mealli and Proserpio. The calculations were made on the basis of atomic coordinates obtained from the single-crystal X-ray data analysis of compound **1**. The results reveal that HOMO-1, HOMO, LUMO and LUMO+1 all are essentially ligand orbitals with (>90% ligand contribution, see Figure S9). Thus the lowest-energy transitions in the present polymeric complexes are ascribed to electronic transitions within the ligand orbitals (π - π^*). Modification of the properties of the ligand orbitals in the present examples is due to increased

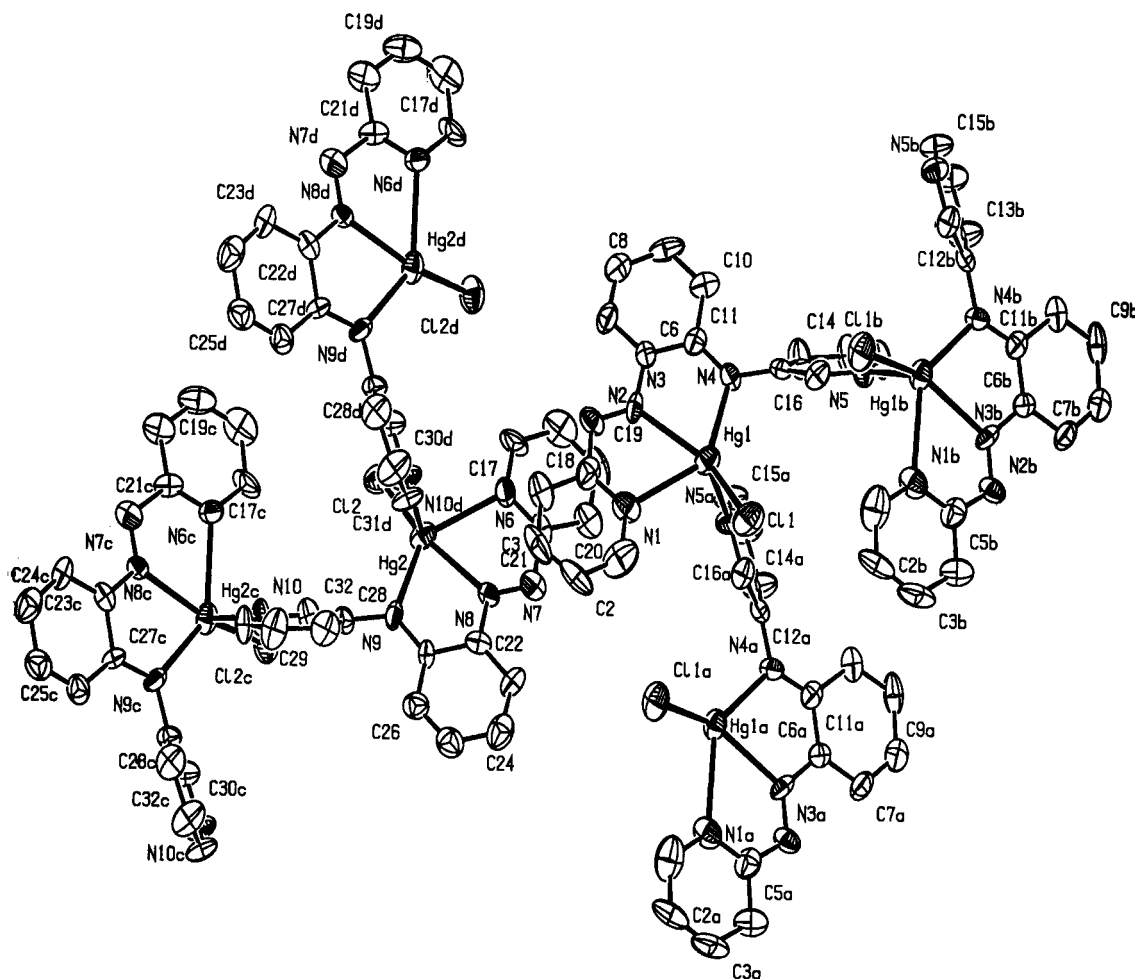
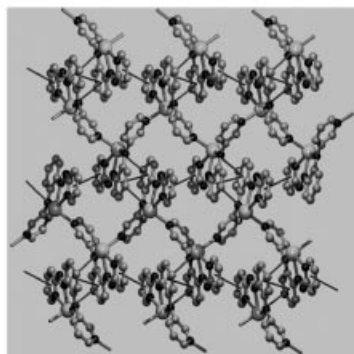


Figure 7. ORTEP and atom-numbering scheme for $[\text{HgCIL}^3]_\infty$. Hydrogen atoms are omitted for clarity.



(a)



(b)

Figure 8. (a) Space-filling model for $[\text{HgCIL}^3]_\infty$, showing the chain that adopts a saw-tooth-like backbone. (b) Different weak interactions constructed by π - π and (Hg) metal- π interactions between the adjacent polymer units running along the a axis.

Table 1. Selected bond lengths [Å] and bond angles [°] for $[\text{HgCIL}^3]_\infty$ (1).

Bond lengths			
Hg(1)–N(1)	2.53(2)	Hg(2)–N(6)	2.50(1)
Hg(1)–N(3)	2.41(1)	Hg(2)–N(8)	2.34(1)
Hg(1)–N(4)	2.27(1)	Hg(2)–N(9)	2.26(1)
Hg(1)–N(5)	2.43(1)	Hg(2)–N(10)	2.40(1)
Hg(1)–Cl(1)	2.40(1)	Hg(2)–Cl(2)	2.40(1)
N(2)–N(3)	1.24(1)	N(7)–N(8)	1.26(1)
N(3)–C(6)	1.41(2)	N(8)–C(22)	1.34(2)
C(6)–C(11)	1.40(2)	C(22)–C(27)	1.46(2)
C(11)–N(4)	1.31(2)	C(27)–N(9)	1.36(2)
N(4)–C(12)	1.42(2)	N(9)–C(28)	1.39(2)
Bond angles			
N(3)–Hg(1)–N(4)	71.7(5)	N(1)–Hg(1)–N(3)	63.0(5)
N(9)–Hg(2)–N(8)	70.5(4)	N(8)–Hg(2)–N(6)	66.2(4)

planarity of the ligand and also to extensive charge delocalization along the ligand backbone. A similar type of finding was reported recently on the Zn^{II} and Cd^{II} complexes^[24,25] of heterocyclic ligands. In such systems, heteroatoms decrease the π and π^* orbital energies considerably, and as a result, the HOMO and LUMO lack contribution from the metal atoms. In addition, multiple electronic transitions are

Table 2. Crystallographic data for complex **1**.

Complex	[C ₁₆ H ₁₂ ClHgN ₅] _∞
Empirical formula	C ₁₆ H ₁₂ ClHgN ₅
Molecular mass	510.35
<i>T</i> [K]	295(2)
Crystal system	orthorhombic
Space group	<i>Pca</i> 2 ₁
Wavelengths [Å]	0.71073
<i>a</i> [Å]	10.1452(5)
<i>b</i> [Å]	18.1918(9)
<i>c</i> [Å]	17.3237(9)
<i>α</i> [°]	90.00
<i>β</i> [°]	90.00
<i>γ</i> [°]	90.00
<i>V</i> [Å ³]	3197.3(3)
<i>Z</i>	8
<i>D</i> _{calcd.} [g cm ⁻³]	2.120
Crystal dimension [mm]	0.20 × 0.10 × 0.02
<i>θ</i> range for data collection [°]	1.12–27.50
GOF on <i>F</i> ²	1.042
Reflections collected	29113
Unique reflections	7341
Final <i>R</i> indices [<i>I</i> > 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0595, <i>wR</i> ₂ = 0.0947
Largest diff. between peak and hole [e Å ⁻³]	0.974, −1.466

Table 3. π – π interactions (face-to-face) in complex **1**.

ring(<i>i</i>) → ring(<i>j</i>)	Dihedral angle between ring planes (<i>i,j</i>) [°]	Angle between first ring normal and the line joining ring Cg's (<i>i,j</i>) [°]	⊥ distance of centroid(<i>i</i>) from ring(<i>j</i>) [Å]
R(1) → R(2) ^[a]	4.16	39.02	3.441
R(3) → R(4) ^[b]	1.70	40.29	3.451

[a] Symmetry code: = 1 + *x*, *y*, *z*. [b] Symmetry code: = *x*, *y*, *z*.

Table 4. (Hg) metal– π ring interactions in complex **1**.^[a]

R(<i>i</i>)–Hg(<i>j</i>)	Metal-to-Cg distance [Å]	Angle between joining line and ring normal [°]
R(3)–Hg(2)	3.373	24.08
R(4)–Hg(1)	3.412	26.63

[a] Where R(1) represents N1–C1–C2–C3–C4–C5; R(2) represents N6–C17–C18–C19–C20–C21; R(3) represents C6–C7–C8–C9–C10–C11; R(4) represents C22–C23–C24–C25–C26–C27.

also noted in the high-energy region. Spectral data of **1** and **2** are presented in the Experimental Section, and the spectra are shown in Figure 9.

The emission properties of the complexes were studied in the solid state at room temperature. The emission spectra are found to be dependent on the excitation wavelength. For example, the mercury complex **1** shows a relatively weak emission band at 690 nm upon excitation at 640 nm. Interestingly, multiple blue-green emission bands with maxima at 420, 450 and 485 nm are observed upon excitation at 335 nm, whereas emission bands with maxima at 425 nm and 460 nm are observed upon excitation with the very short wavelength of 235 nm. Multiple emission bands were reported^[26] previously in other d¹⁰ metal complexes. A similar behaviour in the emission spectrum of the corresponding zinc complex is also observed. The emission spectra of the mercury MOF are displayed in Figure 10, whereas the

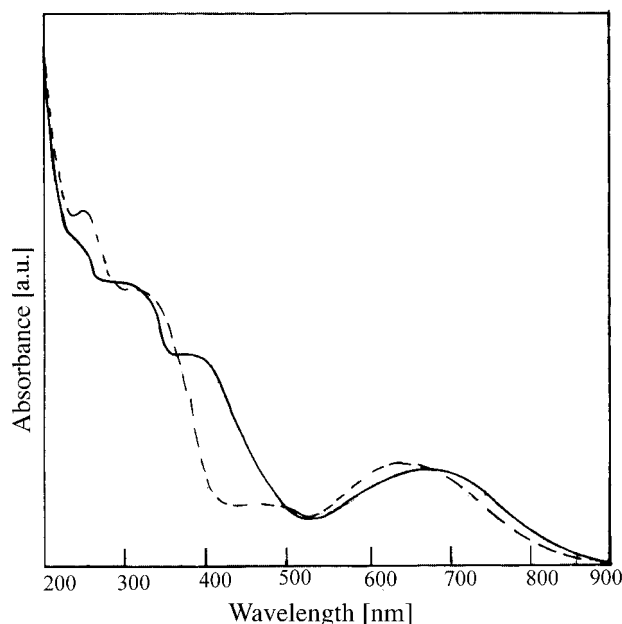


Figure 9. An overlay of UV/Vis spectra for the two MOFs in the solid state: (i) [HgCIL₃]_∞ (----), (ii) [ZnCIL₃·3H₂O]_∞ (—).

emission spectra of its Zn analogue have been submitted as Supporting Information (Figure S10). It should be noted that the ligand [HL³] shows very weak luminescence in the solid state upon excitation at 255 and 335 nm. The photo-physical properties of complexes **1** and **2** are unique in the sense that no other reported compound of this and similar azo-aromatic ligands exhibit detectable luminescence. The luminescence properties in these examples thus may be attributed to the^[27–28] polymeric nature of the complexes. This imparts rigidity in the ligand framework and thus reduces energy loss through a nonradiative relaxation pathway. In this context, it should be noted that blue-green luminescent coordination complexes have been studied intensively because of their possible applications in material science.^[29]

Sorption Properties

The presence of peaks at low *2θ* range in the XRPD pattern of the above polymers suggest that the possible ordering of the building units of these functional materials^[30] is similar to that of microporous^[31] systems. Whereas the Zn complex indeed shows the moderate ability of adsorption of small molecules like N₂ and H₂, its Hg^{II} analogue shows poor adsorption ability.

The N₂ sorption experiment on the Zn polymer **2** at 77 K suggests a type I isotherm at low *P/P*₀ ratio of N₂ that corresponds to the presence of micropores with a BET surface area of 214 m² g^{−1}. Pore size distribution of the sample, obtained by using Horvath–Kawazoe method,^[32] is shown in Figure 11. Two broad maxima can be seen at 9.2 and 14.1 Å in the micropore region. The average pore diameter of 9.2 Å can be explained from the low-range *2θ* peaks in the powder XRD pattern (Figure 5). The pore diameter of this sample

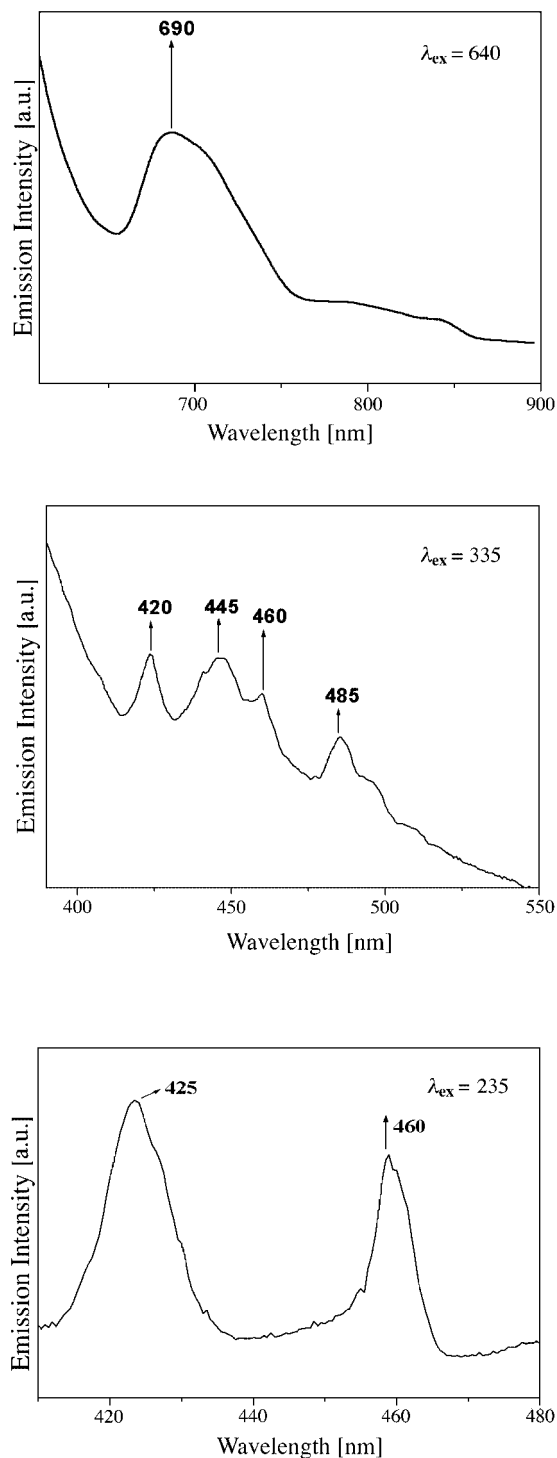


Figure 10. Multiple emission spectra for $[\text{HgCIL}^3]_\infty$ at different excitation wavelengths.

estimated from the TEM analysis (vide supra) [Figure 6] agrees well with the N_2 sorption data. The presence of the peak at a pore diameter of $14.1 \text{ \AA}$ may be attributed to the large micropores generated at the interparticle cages. We have also carried out H_2 sorption on the reference Zn polymer. The H_2 adsorption/desorption isotherm at 77 K is shown in Figure 12. The nature of the isotherms suggests

complete reversible adsorption and desorption for H_2 , and a steady increment in the uptake of H_2 with increasing pressure.

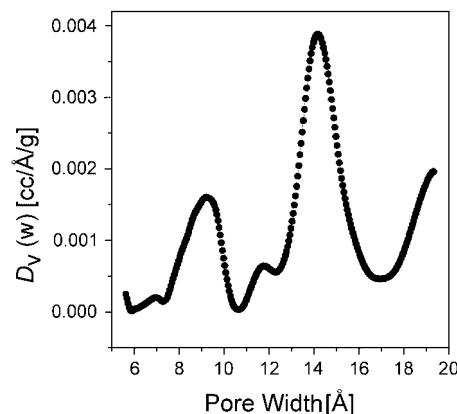


Figure 11. Pore size distribution curve for $[\text{ZnCIL}^3 \cdot 3\text{H}_2\text{O}]_\infty$.

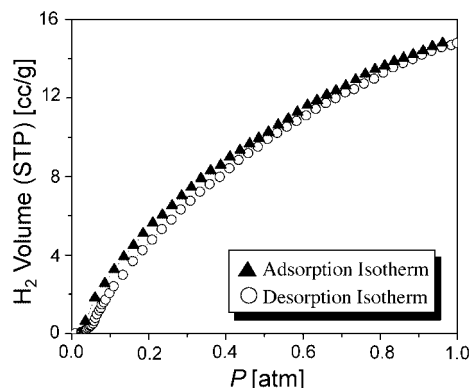


Figure 12. Isotherms for the adsorption and desorption of H_2 gas for $[\text{ZnCIL}^3 \cdot 3\text{H}_2\text{O}]_\infty$.

The observed BET surface area of the mercury polymer is small, $13.5 \text{ m}^2\text{g}^{-1}$, and is quite low relative to that of the zinc sample. This indicates that nitrogen gas adsorption occurs primarily at the external surface of the mercury polymer and that the adsorbate nitrogen molecule cannot freely diffuse into the internal channels of this solid, as observed for other microporous solids.^[33]

Thermogravimetric (TGA) analyses of samples **1** and **2** were performed to estimate the stability of the complexes at elevated temperatures. Figure S11 in the Supporting Information shows the TGA curves for samples **1** and **2**. The mercury sample **1** is stable only up to 97°C . A continuous weight loss ($>35\%$) followed by another massive weight loss of ($>50\%$) are noted in the temperature range $100\text{--}225^\circ\text{C}$ and $225\text{--}375^\circ\text{C}$, respectively. The weight loss in the temperature range $100\text{--}225^\circ\text{C}$ may be attributed to the loss of the ligand, 2-(phenylazo)pyridine. In comparison, the Zn polymer **2** shows a slow weight loss of 7.2% in the range $25\text{--}275^\circ\text{C}$, which is attributed to the loss of adsorbed water. Between 275°C and 325°C , there are multiple stages of

weight loss, which amount to 14.4%, presumably due to the loss of water present from the large micropore region. A weight loss of 11.1% in the range 325–370 °C and of 14.0% in the range 370–500 °C, as a result of the collapse of the metal–ligand framework, is observed. We wish to note here that the Zn–L³ framework remains intact up to 325 °C, as evidenced by their near identical XRPD pattern; above this temperature, the network collapses.

Conclusions

In this work we have described the isolation and characterization of a polymeric network of Zn^{II} and Hg^{II} with a designed azo-aromatic ligand. The gradual growth of the particles of the polymeric materials has been followed by successive product isolation at different time intervals. Unusually, the polymers are blue-green, have five-coordinate metal centres and display emission in the blue-green region of the visible spectrum. The Zn polymer is microporous and its sorption isotherm is reversible. Our work in the area of designing multifunctional azo-aromatic bridging ligands continues.

Experimental Section

Materials: The starting complex [Co(pap)₃](ClO₄)₂ was prepared by a reported procedure.^[34] The salts ZnCl₂ and HgCl₂ were obtained from Merck India Limited and Qualigens, respectively. 3-Aminopyridine was obtained from S.D. Fine-chemical Limited. Solvents and chemicals used for synthesis were of analytical grade.

Physical Measurements: A JASCO V-570 Spectrophotometer was used to record electronic spectra. The IR spectra were recorded with a Perkin–Elmer 783 spectrophotometer. ¹H NMR spectra were measured in CDCl₃ with a Bruker Avance DPX 300 spectrometer, and SiMe₄ (TMS) was used as the internal standard. A Perkin–Elmer 240C elemental analyzer was used to collect microanalytical data (C, H and N). The compositional analyses were evaluated by energy dispersive spectroscopy (EDS). Microstructures of the nano forms were studied by scanning electron microscopy (SEM, Hitachi S-3200), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM, JEOL JEM 2010 TEM at an accelerating voltage of 200 kV). Solid state emission spectra were recorded at room temperature at different excitation wavelengths with a Perkin–Elmer LS 55 Luminescence Spectrometer. ESI mass spectra were recorded on a micro-mass Q-TOF mass spectrometer (serial no. YA-263). Powder XRD data were recorded on a Seifert 3000P diffractometer, on which small- and wide-angle goniometers were mounted, at 40 kV and 20 mA by using Cu-K_α radiation (λ = 1.5406 Å) with a scan speed of 2° min^{−1}. Sorption isotherm studies were performed by using a Quantachrome AUTOSORB 1C-TCD sorption instrument at 77 K. Prior to gas adsorption measurements, samples were degassed for 2 h at 100 °C for **1** and at 120 °C for **2** to remove all guest molecules. Thermogravimetric (TGA) analyses for the representative samples were conducted at a scan rate of 5.00 °C min^{−1} by using a Perkin–Elmer DIAMOND TG/DTA thermogravimeter. Melting points were determined with the help of a capillary fitting Mel. Temp. II (Laboratory Devices Inc., USA) apparatus.

Synthesis of Compounds

HL³ Synthesis: Two steps were involved: (i) *ortho*-amination on [Co(pap)₃]²⁺ followed by (ii) ligand isolation from the cobalt complex.

Isolation of [Co(L³)₂](ClO₄) from [Co(pap)₃](ClO₄)₂: A mixture of [Co(pap)₃](ClO₄)₂ (0.2 g, 0.25 mmol) and 3-aminopyridine (0.1 g, 1.06 mmol) was heated on a steam bath for 7 h. The initial brown colour gradually became intense green. The crude product, which contained mainly the compound [Co(L³)₂](ClO₄), was further purified on a preparative TLC plate (silica gel) with a acetonitrile/chloroform mixture (1:4) as eluent. A yellowish band of unreacted 3-aminopyridine moved first, followed by a major green band of the cobalt compound [Co(L³)₂](ClO₄). The major green band was collected and was thoroughly washed with diethyl ether. Crystalline pure green [Co(L³)₂](ClO₄) was obtained from a dichloromethane/hexane mixture. Yield: 0.125 g, 70%. ESI-MS: *m/z* = 607.15 [M – ClO₄][−]. C₃₂H₂₄ClCoN₁₀O₄ (706.93): calcd. C 54.36, H 3.42, N 19.81; found C 54.40, H 3.40, N, 19.75. IR (KBr): $\tilde{\nu}$ = 1600 (s) [C=N], 1325 (vs) [N=N], 1085 (s), 620 (s) [ClO₄][−] cm^{−1}. UV/Vis (in dichloromethane, λ_{max}): 315, 400, 720, 790, 880 nm.

Isolation of [3-(2-Pyridylamino)phenyl]azopyridine (HL³) from [Co(L³)₂](ClO₄): The cobalt complex [Co(L³)₂](ClO₄) (0.15 g, 0.21 mmol) was dissolved in ethanol (30 mL), and hydrazine hydrate (5 mL) and yellow ammonium sulfide (5 mL) were added. The mixture was then stirred for 30 min at room temperature. The resulting orange-yellow solution was evaporated to dryness, and the product was extracted with dichloromethane and loaded on a preparative TLC plate (silica gel) for purification. An orange-yellow band was eluted with a toluene/chloroform mixture (2:1), which on evaporation yielded orange crystals of HL³. Yield: 0.075 g, 65%. M.p. 98 °C. ESI-MS: *m/z* = 276.10. p*K*_a = 8.7 ± 0.1. C₁₆H₁₃N₅ (275.28): calcd. C 69.81, H 4.75, N 25.44; found. C 69.75, H 4.80, N 25.40. IR (KBr): $\tilde{\nu}$ = 1585 (s) [C=N], 1315 (vs) [N=N] cm^{−1}. UV/Vis (solid, λ_{max}): 255, 335, 460 nm.

Polynuclear Mercury(II) Complex [HgCIL³]_∞ (1): In a long neck crystal tube, an aqueous solution (5 mL) containing HgCl₂ (100 mg, 0.365 mmol), water (2 mL) and a methanolic solution of a mixture of HL³ (100 mg, 0.365 mmol) and of NEt₃ (2 drops) were layered gradually in the above order. In between the water and methanol solvent layer, a green ring formed almost immediately. The tube was stoppered and left undisturbed at room temperature. Slow diffusion between the two solutions afforded dark green crystals of complex **1** after 3 weeks. Yield: 0.130 g, 70%. C₁₆H₁₂ClHgN₅ (510.32): calcd. C 37.66, H 2.37, N 13.72; found C 37.65, H 2.39, N 13.67. IR (KBr): $\tilde{\nu}$ = 1590 (s) [C=N], 1300 (vs) [N=N] cm^{−1}. UV/Vis (solid, λ_{max}): 245, 345, 500, 660 nm.

The growth process of the mercury particles was followed by carrying out the synthetic reaction in five sealed tubes (A–E) by using an identical reaction mixture as stated above but by varying the reaction time. The samples were collected after 5 h, 36 h, 5 d, 10 d and 21 d.

Polynuclear Zinc(II) Complex [ZnCIL³·3H₂O]_∞ (2): In a long neck crystal tube, the deprotonated methanolic ligand solution of [L³][−] (100 mg, 0.365 mmol) was layered over a methanolic solution of ZnCl₂ (50 mg, 0.365 mmol). The tube was stoppered and left undisturbed at room temperature. A dark polycrystalline complex of the zinc polymer was isolated from the tube after 6 d. Yield: 0.125 g, 80%. C₁₆H₁₈ClN₅O₃Zn (429.16): calcd. C 44.77, H 4.22, N 16.31; found C 44.70, H 4.22, N 16.26. IR (KBr): $\tilde{\nu}$ = 1595 (s) [C=N], 1310 (vs) [N=N], 3440 (s) [H₂O] cm^{−1}. UV/Vis (solid, λ_{max}): 255, 335, 380, 675 nm.

X-ray Crystallography: Crystallographic data for compound **1** is collected in Table 2. Specific details are given below.

[HgCIL³]_∞ (1): Suitable X-ray quality crystals (0.20 × 0.10 × 0.02 mm) of [HgCIL³]_∞ (**1**) were obtained by layering an aqueous solution of HgCl₂ over an aqueous solution of the deprotonated ligand [L³][−] in a crystal tube, as described above. Suitable crystals were obtained after 3 weeks from the tube. X-ray data were collected on a Bruker SMART diffractometer equipped with Mo-*K*_α radiation ($\lambda = 0.71073$ Å) and were corrected for Lorentz-polarisation effects. A total of 29113 reflections were collected, of which 7341 were unique ($R_{\text{int}} = 0.0990$) and were used in subsequent analysis. The structure was solved by employing the SHELXS-97 program package^[35a,35b] and refined by full-matrix least-squares based on F^2 (SHELXL-97).^[35c] Crystallographic graphics were obtained by using the programs ORTEP^[36] and PLATON.^[37] CCDC-621241 (for **1**) contains 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.

Supporting Information (see footnote on the first page of this article): ESI-MS spectrum of ligand [H₂L³]⁺, ¹H- and ¹³C NMR spectra for HL³ and [Co(L³)₂]⁺, powder X-ray diffraction analysis for amorphous complex **1**, photoluminescence spectra for complex **2**, energy dispersive spectra for complexes **1** and **2**, semiempirical EHMO calculation of complex **1**, and TGA curve for complexes **1** and **2** are available.

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- [1] a) B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.* **1990**, *112*, 1546–1554; b) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117–138; c) B. Moulton, M. J. Zawarko, *Chem. Rev.* **2001**, *101*, 1629–1658; d) R. Kitaura, K. Fujimoto, S. Noro, M. Kondo, S. Kitagawa, *Angew. Chem. Int. Ed.* **2002**, *41*, 133–135; e) C. Janiak, *Dalton Trans.* **2003**, 2781–2804; f) Y. Xiong, Yi. Xie, S. Chen, Z. Li, *Chem. Eur. J.* **2003**, *9*, 4991–4996; g) B. Liu, D.-J. Qian, H.-X. Huang, T. Wakayama, S. Hara, W. Huang, C. Nakamura, J. Miyake, *Langmuir* **2005**, *21*, 5079–5084; h) M. Oh, C. L. Stern, C. A. Mirkin, *Inorg. Chem.* **2005**, *44*, 2647–2653; i) M. Oh, C. A. Mirkin, *Nature* **2005**, *438*, 651–654.
- [2] a) X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, A. P. Alivisatos, *Nature* **2000**, *404*, 59–61; b) C. Ye, G. Meng, Y. Wang, Z. Jiang, L. Zhang, *J. Phys. Chem. B* **2002**, *106*, 10338–10341; c) Z.-X. Deng, C. Wang, X.-M. Sun, Y.-D. Li, *Inorg. Chem.* **2002**, *41*, 869–873; d) X. Chen, H. Xu, N. Xu, F. Zhao, W. Lin, G. Lin, Y. Fu, Z. Huang, H. Wang, M. Wu, *Inorg. Chem.* **2003**, *42*, 3100–3106; e) Q. Peng, S. Xu, Z. Zhuang, X. Wang, Y. Li, *Small* **2005**, *1*, 216–221; f) S. Biswas, S. Kar, S. Chaudhuri, *J. Phys. Chem. B* **2005**, *109*, 17526–17530; g) S. Kar, S. Chaudhuri, *J. Phys. Chem. B* **2005**, *109*, 3298–3302; h) S. Kar, B. N. Pal, S. Chaudhuri, D. Chakravorty, *J. Phys. Chem. B* **2006**, *110*, 4605–4611; i) S. Kar, S. Chaudhuri, *J. Phys. Chem. B* **2006**, *110*, 4542–4547.
- [3] a) T. Uemura, S. Kitagawa, *J. Am. Chem. Soc.* **2003**, *125*, 7814–7815; b) X. Zhang, Y. Xie, W. Yu, Q. Zhao, M. Jiang, Y. Tian, *Inorg. Chem.* **2003**, *42*, 3734–3737; c) M. Yamada, M. Arai, M. Kurihara, M. Sakamoto, M. Miyake, *J. Am. Chem. Soc.* **2004**, *126*, 9482–9483.
- [4] a) S. Vaucher, M. Li, S. Mann, *Angew. Chem. Int. Ed.* **2000**, *39*, 1793–1796; b) S. Vaucher, J. Fielden, M. Li, E. Dujardin, S. Mann, *Nano Lett.* **2002**, *2*, 225–229; c) G. Larsen, R. V. Ortiz, K. Minchow, A. Barrero, I. G. Loscertales, *J. Am. Chem. Soc.* **2003**, *125*, 1154–1155; d) E. Y. Lee, S. Y. Jang, M. P. Suh, *J. Am. Chem. Soc.* **2005**, *127*, 6374–6381.
- [5] a) S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494; b) A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem. Int. Ed.* **1999**, *38*, 3268–3292; c) D. Hargman, P. J. Hagrman, J. Zubietta, *Angew. Chem. Int. Ed.* **1999**, *38*, 3165–3168; d) S. S.-Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148–1150; e) J.-C. Dai, X.-T. Wu, Z.-Y. Fu, C.-P. Cui, S.-M. Hu, W.-X. Du, L.-M. Wu, H.-H. Zhang, R.-Q. Sun, *Inorg. Chem.* **2002**, *41*, 1391–1396.
- [6] a) A. Mederos, S. Domínguez, R. Hernández-Molina, J. Sanchiz, F. Brito, *Coord. Chem. Rev.* **1999**, *193–195*, 913–939; b) A. Mederos, S. Domínguez, R. Hernández-Molina, J. Sanchiz, F. Brito, *Coord. Chem. Rev.* **1999**, *193–195*, 857–911; c) Md. B. Zaman, M. D. Smith, D. M. Ciurtin, H.-C. zur Loye, *Inorg. Chem.* **2002**, *41*, 4895–4903 and reference herein; d) X. Xue, X.-S. Wang, L.-Z. Wang, R.-G. Xiong, B. F. Abrahams, X.-Z. You, Z.-L. Xue, C.-M. Che, *Inorg. Chem.* **2002**, *41*, 6544–6546; e) D. M. Shin, I. S. Lee, Y.-A. Lee, Y. K. Chung, *Inorg. Chem.* **2003**, *42*, 2977–2982; f) Y.-B. Dong, X. Zhao, R.-Q. Huang, M. D. Smith, H. C. zur Loye, *Inorg. Chem.* **2004**, *43*, 5603–5612; g) A. Cingolani, S. Galli, N. Masciocchi, L. Pandolfo, C. Pettinari, A. Sironi, *J. Am. Chem. Soc.* **2005**, *127*, 6144–6145.
- [7] a) Y. Cui, H. L. Ngo, W. Lin, *Inorg. Chem.* **2002**, *41*, 1033–1035; b) Z.-Y. Fu, X.-T. Wu, J.-C. Dai, S.-M. Hu, W.-X. Du, H.-H. Zhang, R.-Q. Sun, *Eur. J. Inorg. Chem.* **2002**, 2730–2735; c) S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276–288; d) G. Férey, M. Latroche, C. Serre, F. Millange, T. Loiseau, A. P. Guégan, *Chem. Commun.* **2003**, 2976–2977; e) X. Wang, C. Qin, E. Wang, Y. Li, N. Hao, C. Hu, L. Xu, *Inorg. Chem.* **2004**, *43*, 1850–1856.
- [8] J. Otsuki, N. Omokawa, K. Yoshida, I. Yoshikawa, T. Akasaka, T. Suenobu, T. Takido, K. Araki, S. Fukuzumi, *Inorg. Chem.* **2003**, *42*, 3057–3066.
- [9] a) S. Hvilsted, F. Andruzzi, P. S. Ramanujam, *Opt. Lett.* **1992**, *17*, 1234–1236; b) P. S. Ramanujam, S. Hvilsted, I. Zebger, F. Andruzzi, *Appl. Phys. Lett.* **1993**, *62*, 1041–1043; c) P. S. Ramanujam, S. Hvilsted, I. Zebger, H. W. Siesler, *Macromol. Rapid Commun.* **1995**, *16*, 455–461; d) G. J. Lee, D. Kim, M. Lee, *Appl. Opt.* **1995**, *34*, 138–143; e) I. Willner, S. Rubin, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 367–385; f) N. Zheng, X. Bu, P. Feng, *J. Am. Chem. Soc.* **2002**, *124*, 9688–9689.
- [10] a) A. Saha, A. K. Ghosh, P. Majumdar, K. N. Mitra, S. Mondal, K. K. Rajak, L. R. Falvello, S. Goswami, *Organometallics* **1999**, *18*, 3772–3774; b) A. Saha, P. Majumdar, S.-M. Peng, S. Goswami, *Eur. J. Inorg. Chem.* **2000**, 2631–2639; c) A. Saha, P. Majumdar, S. Goswami, *J. Chem. Soc., Dalton Trans.* **2000**, 1703–1708; d) C. Das, A. K. Ghosh, C.-H. Hung, G.-H. Lee, S.-M. Peng, S. Goswami, *Inorg. Chem.* **2002**, *41*, 7125–7135; e) C. Das, A. Saha, C.-H. Hung, G.-H. Lee, S.-M. Peng, S. Goswami, *Inorg. Chem.* **2003**, *42*, 198–204.
- [11] A. Sanyal, P. Banerjee, G.-H. Lee, S.-M. Peng, C.-H. Hung, S. Goswami, *Inorg. Chem.* **2004**, *43*, 7456–7462.
- [12] a) K. K. Kamar, S. Das, C.-H. Hung, A. Castiñeiras, M. D. Kuzmin, C. Rillo, J. Bartolomé, S. Goswami, *Inorg. Chem.* **2003**, *42*, 5367–5375; b) S. Das, C.-H. Hung, S. Goswami, *Inorg. Chem.* **2003**, *42*, 5153–5157; c) S. Das, C.-H. Hung, S. Goswami, *Inorg. Chem.* **2003**, *42*, 8592–8597; d) S. Das, S.-M. Peng, G.-H. Lee, S. Goswami, *Ind. J. Chem. Sect. A* **2005**, *44A*, 1561–1564.
- [13] S. Das, P. Banerjee, S.-M. Peng, G.-H. Lee, J. Kim, S. Goswami, *Inorg. Chem.* **2006**, *45*, 562–570.
- [14] Metal ions that have a preference for hexacoordination, for example Co^{III}, Ni^{II} etc., produce monometallic complexes of

- the type $[M(L^3)_2]^{n+}$, where the 3-pyridyl nitrogen atom of the ligand remains^[15] uncoordinated. There are strong indications that suggest that these complexes might be useful building blocks for the construction of heterometallic systems.
- [15] P. Banerjee, S.-M. Peng, G.-H. Lee, S. Goswami, unpublished results.
- [16] a) K. Kobashi, K. Nishimura, Y. Kawate, T. Horiuchi, *Phys. Rev. B* **1988**, *38*, 4067–4084; b) Ch. Wild, N. Herres, P. Koidl, *J. Appl. Phys.* **1990**, *68*, 973–978; c) M. A. Tamor, M. P. Everson, *J. Mater. Res.* **1994**, *9*, 1839–1848; d) C. Ye, G. Meng, Y. Wang, Z. Jiang, L. Zhang, *J. Phys. Chem. B* **2002**, *106*, 10338–10341.
- [17] M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reinke, M. O’Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330.
- [18] a) L. Pauling, R. B. Corey, *Chemistry* **1953**, *39*, 253; b) M. L. Mansfield, *J. Phys. Chem.* **1989**, *93*, 6926–6928.
- [19] A. W. Addison, T. N. Rao, J. Reedijk, J. V. Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.
- [20] a) A. E. Mauro, S. H. Pulcinelli, R. H. A. Santos, M. T. P. Gambardella, *Polyhedron* **1992**, *11*, 799–803; b) D. C. Bebout, D. E. Ehmann, J. C. Trinidad, K. K. Crahan, M. E. Kastner, D. A. Parrish, *Inorg. Chem.* **1997**, *36*, 4257–4264; c) D. C. Bebout, M. M. Garland, G. S. Murphy, E. V. Bowers, C. J. Abelt, R. J. Butcher, *Dalton Trans.* **2003**, 2578–2584 and references cited therein.
- [21] a) M. Enders, G. Ludwig, H. Pritzkow, *Eur. J. Inorg. Chem.* **2002**, 539–542 and references therein; b) Z. D. Tomic, V. M. Leovac, Ž. K. Jaćimović, C. Giester, S. D. Zarić, *Inorg. Chem. Commun.* **2006**, *9*, 833–835.
- [22] a) P. Pykkö, *Chem. Rev.* **1997**, *97*, 597–636; b) P. Pykkö, M. Straka, *Phys. Chem. Chem. Phys.* **2000**, *2*, 2489–2494.
- [23] C. Mealli, D. M. Proserpio, *J. Chem. Educ.* **1990**, *67*, 399–402.
- [24] S.-L. Zheng, J.-H. Yang, X.-L. You, X.-M. Chen, W.-T. Wong, *Inorg. Chem.* **2004**, *43*, 830–838.
- [25] S.-L. Zheng, J.-P. Zhang, X.-M. Chen, Z.-L. Huang, Z.-Y. Lin, W.-T. Wong, *Chem. Eur. J.* **2003**, *9*, 3888–3896.
- [26] a) M. A. Omary, M. A. Rawashdeh-Omary, H. V. K. Diyabalanage, H. V. R. Dias, *Inorg. Chem.* **2003**, *42*, 8612–8614; b) X. Shi, G. Zhu, X. Wang, G. Li, Q. Fang, G. Wu, G. Tian, M. Xue, X. Zhao, R. Wang, S. Qiu, *Cryst. Growth Des.* **2005**, *5*, 207–213; c) R.-Q. Fang, X.-M. Zhang, *Inorg. Chem.* **2006**, *45*, 4801–4810.
- [27] S.-L. Zheng, M.-L. Tong, S.-D. Tan, Y. Wang, J.-X. Shi, Y.-X. Tong, H.-K. Lee, X.-M. Chen, *Organometallics* **2001**, *20*, 5319–5325.
- [28] a) B. Valuer, *Molecular Fluorescence: Principle and Applications*, Wiley-VCH, Weinheim, **2002**; b) A. W. Adamson, P. D. Fleischauer, *Concept of Inorganic Photochemistry*, John Wiley & Sons, New York, **1975**; c) H. Yersin, A. Vogler (Eds.), *Photochemistry and Photophysics of Coordination Compounds*, Springer-Verlag, Berlin, **1987**.
- [29] J. Tao, M.-L. Tong, J.-X. Shi, X.-M. Chen, S. W. Ng, *Chem. Commun.* **2000**, 2043–2044.
- [30] B. Chen, M. Eddaoudi, S. T. Hyde, M. O’Keeffe, O. M. Yaghi, *Science* **2001**, *291*, 1021–1023.
- [31] R. Szostak, *Molecular Sieves: Principles of Synthesis and Identification*, Van Nostrand Reinhold, New York, **1989**.
- [32] G. Horvath, K. Kawazoe, *J. Chem. Eng. Jpn.* **1983**, *16*, 470–475.
- [33] M. Du, Z.-H. Zhang, X.-J. Zhao, Q. Xu, *Inorg. Chem.* **2006**, *45*, 5785–5792.
- [34] A. K. Mahapatra, Ph. D. Thesis, Jadavpur University, Calcutta, India, **1986**.
- [35] a) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473; b) G. M. Sheldrick, *SHELXS-97, Program for the Solution of the Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**; c) G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.
- [36] C. K. Johnson, *ORTEP II*, Report ORNL-5138, Oak Ridge National Laboratory, TN, USA, **1976**.
- [37] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **1999**.

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