The trans-Bis(p-thioetherphenylacetynyl)bis(phosphine)platinum(II) Ligands: A Step Towards Predictability and Crystal Design

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Supporting Information

ABSTRACT: Two organometallic ligands L1 (trans-[p-MeSC6H4C=C-Pt(PR3)2-C≡CC6H4SMe; R = Me]) and L2 (R = Et) react with CuX salts (X = Cl, Br, I) in MeCN to form one-dimensional (1D) or two-dimensional (2D) coordination polymers (CPs). The clusters formed with copper halide can either be step cubane Cu4X4, rhomboids Cu4X4, or simply CuI. The formed CPs with L1, which is less sterically demanding than L2, exhibit a crystallization solvent molecule (MeCN), whereas those formed with L2 do not incorporate MeCN molecules in the lattice. These CPs were characterized by X-ray crystallography, thermogravimetric analysis, IR, Raman, absorption, and emission spectra, as well as photophysical measurements in the presence and absence of crystallization MeCN molecules for those CPs with the solvent in the lattice (i.e., [(Cu4I4)L1·MeCN], (CP1), [(Cu4Br4)L1·2MeCN]n, (CP3), and [(Cu4I4)L1·MeCN]n, (CP5)). The crystallization molecules were removed under vacuum to evaluate the porosity of the materials by Brunauer–Emmett–Teller (N2 at 77 K). The 2D CP shows a reversible 1 adsorption isotherm for both CO2 and N2, indicative of microporosity, whereas the 1D CPs do not capture more solvent molecules or CO2.

INTRODUCTION

The use of organometallic ligands for the synthesis of coordination polymers (CPs) and metal-organometallic frameworks (MOFs), mostly aimed at catalytic purposes, has been the topic of a relatively recent interest. In parallel, the incorporation of S-containing moieties into organometallic fragments has been a long-standing approach in ligand design,4 and sulfur-containing organics are also well known to assemble Cu(I)-containing species to form one-dimensional (1D), two-dimensional (2D), and three-dimensional coordination polymers.4 Concurrently, the use of the rigid and readily modulable trans-bisacetynylplatinum(II) synthon −C6H4C≡C−Pt(PR3)2−C≡CC6H4− (R = simple alkyls or aryls) [Pt] for the preparation of organometallic polymers has been thoroughly investigated in the past decades, mostly to shine light on their photonic and electrochemical properties and to design light-harvesting and light-emitting materials.5-9 The approach of anchoring of a S-containing residue onto a [Pt] scaffold has been recently performed and used to prepare 2D networks containing Ag nanoparticles.10 The strategy in this case was to generate the corresponding dithioketals,11 which exhibit a different affinity with metals in comparison to the softer thioethers. These materials were not designed for their ability to capture small molecules like MOFs but rather to exploit their assembling ability10 and electronic conductivity.11

In a recent study on 1D and 2D coordination polymers generated by luminescent CuI clusters and flexible R6Cu2S(C6H4S)2, the presence of macrocycles within their framework has been revealed.12 Despite their low porosity, these materials exhibit the reversible removal of small molecules, such as nitriles, MeOH, and CO2, suggesting that they somewhat act like MOFs. However, the major challenge for these materials is that the combination of mono- and dithioethers with CuX salts (X = Cl, Br, I, CN) stubbornly leads to a complete unpredictability of the outcome of the Cu cluster acting as the node and the dimensionality of the coordination polymer.4

We now report the design of two series of coordination polymers prepared from CuX salts (X = Cl, Br, I) and trans-MeSC6H4C≡C-Pt(PR3)2−C≡CC6H4SMe (R = Me (L1), Et (L2)) in MeCN, where two trends are observed. First, the dimensionality of the resulting polymers is not affected whether R = Me or Et. Second, the polymers formed with L1 reveal the presence of crystallization MeCN molecules in the lattice, whereas those formed with L2 do not, despite the identical nature of some of these materials (notably [(Cu4X4)L1]n and [(Cu4X4)L2]d; X = Cl, Br).

RESULTS AND DISCUSSION

Synthesis and Structure Description. L1 and L2 differ only by their R group, Me versus Et. On the basis of past experience, such a subtle difference usually leads to a major variability in nature of the copper(I) cluster (often referred to as secondary building unit; SBU) and polymer dimensionality when flexible chains are used in the thioether ligands.4a-c,19 This is not the case for the rigid L1 and L2 with CuX (X = Cl, Br), which lead in all four cases to 1D polymers CP3–CP6 (Scheme 1, Tables 1 and 2, and Figure 1). These materials...
belong to a category of coordination polymers previously reported for the trans-bis(phenylacetylnyl)bis-(triphenylphosphine)platinum(II) complex, where rhomboid-type SBUs are anchored via a $\eta^2$-$\text{C}=$C coordination bonds (Cu$_2$Br$_2$ and Ag$_2$(CF$_3$SO$_3$)$_2$).$^{13,14,15}$ During the course of this study, the X-ray structure of L2 was obtained (SI) and is found to be consistent with that in the literature$^{7,j,16}$ without any further description.

Conclusively, there is a clear selectivity favoring the ethynyl unit over the thioether by the Cu(I) cation. Moreover, L1 bears smaller PMe$_3$ groups comparatively to PEt$_3$ and so the voids left by the former group are compensated by MeCN crystallization molecules. This trend where L1 uses MeCN to

Table 1. Comparison of Selected Structural Features of CP1–CP6

|          | CP1      | CP2      | CP3      | CP4      | CP5      | CP6      |
|----------|----------|----------|----------|----------|----------|----------|
| SBU structure | Cu$_4$I$_4$ | Cu      | Cu$_2$Br$_2$ | Cu$_2$Br$_2$ | Cu$_2$Cl$_2$ | Cu$_2$Cl$_2$ |
| CP dimensionality | 2D | 1D | 1D | 1D | 1D | 1D |
| crystallization mol./[Pt] | MeCN | 2 (MeCN) | MeCN | 2/0 | 2/0 | 2/0 |
| nb of trivalent Cu | 2/2 | 2/0 | 2/0 | 2/0 | 2/0 | 2/0 |
| nb of tetravalent Cu | 2 | 1 | 0 | 0 | 0 | 0 |
| nb of Cu–S bonds | 2 | 1 | 0 | 0 | 0 | 0 |
| nb of Cu–X bonds | 4 | 1 | 2 | 2 | 2 | 2 |
| nb of Cu–($\eta^2$–C≡C) bonds | 2 | 2 | 2 | 2 | 2 | 2 |

Table 2. Bond Distances in the Rhomboid Cu$_x$X$_y$ Units in CP3–CP6

|          | CP3      | CP4      | CP5      | CP6      |
|----------|----------|----------|----------|----------|
| bond     | (Å) | bond     | (Å) | bond     | (Å) | bond     | (Å) |
| Cu$_1$–Cu$_2$ | 3.190(5) | Cu$_1$–Br$_1$#2 | 2.411(4) | Cu$_1$–Cu$_1$ | 3.0989(6) | Cu$_2$–Cu$_2$ | 3.146(1) |
| Cu$_1$–Br$_1$ | 2.423(5) | Cu$_1$–Br$_1$ | 2.462(3) | Cu$_1$–Cl$_1$ | 2.3070(9) | Cu$_3$–Cu$_2$#2 | 2.2806(1) |
| Cu$_1$–Br$_2$ | 2.401(5) | Cu$_1$–Cu$_1$ | 3.289(1) | Cl$_1$–Cl$_1$ | 2.2878(8) | Cl$_3$–Cl$_2$ | 2.3302(1) |
| Cu$_2$–Br$_2$ | 2.418(5) | Cl$_1$–Cl$_1$ | 3.401(1) | Cl$_3$–Cl$_3$ | 3.371(1) | Cl$_3$–Cl$_3$ | 3.371(1) |

($i$) cis-PtCl$_2$(PMe$_3$)$_2$ (L1) and trans-PtCl$_2$(PEt$_3$)$_2$ (L2), NH$_2$Et$_2$, Cul, tetrahydrofuran.
occupy the empty spaces is also noted for CuI salt (i.e., no MeCN in the lattice of CP2; Figure 2, Table 3). However, two drastic differences are noted. First, the dimensionality is 2D for both CPs via the use of S—Cu coordinations. Second, the SBUs used by CP1 and CP2 also differ. The former uses the known step cubane SBU, and the latter material assembles through a mononuclear Cu—I complex. To the best of our knowledge, the use of a single Cu—I SBU is unprecedented in the formation of CPs built upon thioethers and CuX salts (X = Cl, Br, I).

One interesting structural feature is the significant distortion that L1 and L2 experience upon coordination. Indeed, the most notable structural deviations from an ideal geometry are the C=C≡C angles. In L1 and L2, these angles are only within 4° from the linearity, but fall in the range of approximately 153°–169° in CP1–CP6 (Tables 4 and 5). These distortions are also noted in the interplanar C6H4···C6H4 distances. In L1, this distance is 0.88 Å but increases to distances varying from 1.48 to 3.19 Å for CP1 and CP4–CP6. In case of L2, CP2, and CP3, the C6H4 planes of the ligands form dihedral angles with each other.

**Thermal Stability.** The thermogravimetric analysis (TGA) trace of L2 is used as comparison (see SI for traces and data). It exhibits two major weight losses near 260 and 435 °C most likely corresponding to the loss of one PEr3 (exp. ∼15%, calcld = 16%) and one C≡C6H5SMe (exp. ∼26%, calcld = 21%), respectively. These two plateaus represent a “fingerprint” observed in all of the coordination polymers investigated. Neither L1 nor L2 exhibit crystallization molecules based on their X-ray structures and so no weight loss associated with solvent losses is observed (i.e., at lower temperature).

Conversely, the presence of MeCN molecules is evident from the weight losses depicted in the TGA traces for CP1 and CP3 in the vicinity of 100 °C (Figure 3, see SI for data). The expected absence of MeCN in the lattice of CP2, CP4, and CP6 is also obvious by the lack of weight loss in the 25°–200 °C window. In addition, the effect of ν(C≡C) in the two ligands (L1 and L2) on the formation of CPs was monitored using IR and Raman (for L1, CP1, CP3, and CP5) spectroscopy measurements. These values for the IR data are observed to be in the range of ∼2108 cm⁻¹ for L2 CP1–CP6, whereas it was confirmed that the Raman values for L1, CP1, CP3, and CP5 also fall in relatively the same range of ∼2108 cm⁻¹ (see SI).

Surprisingly, CP5 does not show any weight loss associated with the crystallization molecule. This is due to the crystal “instability” of the latter, which exhibit quick evaporation of the solvent crystallization molecules. The X-ray structure was obtained by selecting a suitable crystal in the mother liquor and then dipping it in glue to avoid solvent evaporation. For TGA analysis, the use of glue is obviously impossible and the solvent loss is observed (i.e., at lower temperature).

**Gas Sorption Measurements and Solvent Removal of MeCN in CP1.** Gas sorption isotherms (CO₂ and N₂) of CP1 at low pressure ranging between 0 and 1100 mbar (∼1.1 atm) were measured (Figure 4, bottom). The Brunauer—Emmett—Teller (BET) data reveal that CP1 is weakly porous (Tables 5 and 6; a space-filling model of the X-ray structure is given in the SI). The CO₂ sorption at 273 K and N₂ sorption at 77 K exhibit type 1 isotherms, which again corroborate the presence of microporous materials. Moreover, despite the low surface area

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**Figure 1.** Oak ridge thermal ellipsoid plot (ORTEP) representations of a fragment of the 1D polymers CP3 (top left), CP4 (top right), CP5 (bottom left), and CP6 (bottom right). The thermal ellipsoids are set at 50% probability. Yellow = S, pale purple = Pt, orange = P, brown = Cu, dark red = Br, green = Cl, blue = C, white = H, and purple = N.
of 79.5 m$^2$/g for CP1 upon removal of MeCN, this microporous material is still able to adsorb up to 16.8 cm$^3$/g STP of CO$_2$ at $\sim$1.1 bar. The powder XRD pattern of CP1 directly measured from the resulting solid after the synthesis exhibits a close similarity with the calculated one using X-ray data extracted from the single crystal, thus confirming its identity. Upon removing the solvent under vacuum (as monitored by TGA, Figure 4), the resulting powder XRD pattern exhibits only modest modifications (at 2$\theta$ $\approx$ 10 and 42$^\circ$, Figure 4), indicating that the polymer structure is intact. More importantly, the peak positions (i.e., 2$\theta$ values) remain unaffected within 0.2$^\circ$ upon removing the MeCN. This result indicates that the 2D grid is rather rigid. The reversible removal and reintroduction of the MeCN molecules in the framework of CP1 was also monitored using the chromaticity measurements as it is conveniently found emissive at 298 K (Figure 5). The chromaticity data undergo a slight change upon removing the crystallization molecule (from the purple dot to the black dot).

As shown, the emission spectrum of CP1 is observed to have a featureless broad band with maximum at 585 nm at room temperature. This feature in these CPs has been previously reported by our group and found to originate from the triplet state due to a large Stokes shift between the absorption maximum with the emission peak. In addition, on the basis of the previous DFT and time-dependent density functional

Table 3. Selected Bond Distances for CP1 and CP2 (See Figure 2)

| Bond       | CP1 (Å)  | CP2 (Å)  |
|------------|----------|----------|
| Cu$_1$–Cu$_1$ | 2.8416(9) | Cu$_1$–I$_1$ | 2.544(2) |
| Cu$_2$–Cu$_1$ | 2.8736(8) | Cu$_2$–I$_2$ | 2.550(2) |
| Cu$_1$–I$_1$ | 2.6274(6) | Cu$_1$–S$_1$ | 2.294(4) |
| Cu$_1$–I$_2$ | 2.7409(9) | Cu$_2$–S$_2$ | 2.307(4) |
| Cu$_2$–I$_1$ | 2.5742(6) | Cu$_2$–S$_2$ | 2.307(4) |
| I$_1$–I$_2$  | 2.1903(7) |
| I$_2$–I$_2$  | 4.4712(8) |
| Cu$_1$–S$_1$ | 2.335(1)  |

Table 4. Interplanar C$_6$H$_4$···C$_6$H$_4$ Distances and C–C≡C Angles within L1 and L2

|         | L1       | L2       | CP1   | CP2   | CP3   | CP4   | CP5   | CP6   |
|---------|----------|----------|-------|-------|-------|-------|-------|-------|
| $D$ (planes 1 and 3) (Å) | 0.881    | "       | 2.283 | "     | "     | 3.122 | 1.484 | 3.190 |
| C–C≡C angle (deg) | 176.1    | 176.6    | 159.8 | 169.1 | 161.0 | 155.0 | 163.5 | 155.2 |

*Not measured as the planes are not parallel.*
theory (TDDFT) calculations, the nature of the excited states for CP1 originates from both intra-L1 (intra-ligand ππ* mixed with MLCT; M = Pt, L = π*-C≡CC6H4) and MXLCT (metal-to-ligand charge transfer, Cu4I4→L1; MX = Cu4J4; L = L1).

Upon partial reintroduction of the solvent (∼33% based on TGA data in Figure 4), the chromaticity data expectedly exhibit again a slight modification moving almost in the direction toward its original position in the chromaticity diagram (from the black dot to the turquoise dot) in Figure 5. Thus, CP1 is capable of releasing MeCN (and CO2), but the uptake is difficult (i.e., slow). Even though the uptake is lower than that in many microporous materials, type I adsorption isotherm is observed.

Special Cases of CP3 and CP5. Both materials exhibit MeCN crystallization molecules in their lattices (Figure 1), but TGA analyses indicate that there is no readsorption of the solvent after removal for CP3 (Figure 4, right) and not at all for CP5 when the single crystals are exposed to air for a certain time (SI).

Table 5. Measured Angles between Planes 1, 2, and 3

| planes   | L1 (deg) | L2 (deg) | CP1 (deg) | CP2 (deg) | CP3 (deg) | CP4 (deg) | CP5 (deg) | CP6 (deg) |
|----------|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1 and 2  | 30.22    | 72.88    | 42.64     | 38.65     | 37.27     | 88.47     | 41.74     | 89.67     |
| 2 and 3  | 30.22    | 70.42    | 42.64     | 39.33     | 40.24     | 88.48     | 41.74     | 89.67     |
| 1 and 3  | a        | 2.68     | a         | 2.86      | 3.65      | a         | a         | a         |

“Not measured as the planes 1 and 3 are parallel.

Table 6. Gas Adsorption Data for CP1, CP3, and CP5

| gas     | T (K) | P (mbar) | quantity adsorbed (cm³/g STP) | surface area (m²/g) | pore volume (cm³/g) |
|---------|-------|----------|------------------------------|---------------------|---------------------|
| CP1     | CO₂   | 273      | 1046                         | 16.8                | 79.5                | 0.027               |
|         | N₂    | 77       | 972                          | 2.6                 | 2.3                 | <0.01               |
| CP3     | CO₂   | 273      | 1046                         | 1.9                 | 0.5                 | <0.01               |
|         | N₂    | 77       | 1001                         | b                   | c                   | c                   |
| CP5     | CO₂   | 273      | 1046                         | 1.8                 | 1.3                 | <0.01               |
|         | N₂    | 77       | 994                          | 0.7                 | 0.4                 | <0.01               |

“For CO₂, estimation of the structural parameters was made using density functional theory (DFT) calculations model, whereas for N₂ gas, the surface area was measured from BET. “Too small to be estimated. “Not calculated.

Figure 3. Top: Powder X-ray diffraction (PXRD) patterns of CP1; black = calculated from the single-crystal X-ray data, blue = measured from (crushed) single crystals, and red = after removing the MeCN crystallization molecule under vacuum. Bottom: CO₂ (red; at 273 K) and N₂ (black; at 77 K) sorption isotherms for CP1, measured from single crystals. Closed circles = adsorption; open circles = desorption.

Figure 4. TGA traces focusing on the temperature range where the solvent loss occurs in CP1 (i.e., MeCN) as synthesized, showing solvent loss. Black: CP1 and CP3 were used as single crystals; red: TGA curve after the solvent removal under vacuum; blue: TGA trace after exposition to MeCN vapor. Full TGA traces are provided in the SI. For CP5, the MeCN solvent evaporated too quickly to be observed. The TGA trace is the same as that for the blue and red traces of CP3. We note that CP5 does not exhibit a plateau in this range.
In an attempt to figure out this particular result, CP3 was subjected to necessary crushing for powder XRD analysis, and the resulting pattern turned out to be completely different from the calculated pattern extracted from its X-ray data (Figure 6).

This experiment indicates that CP3 has changed during crushing, a resulting structure exhibiting no crystallization molecules based on the TGA traces (Figures 4). In an attempt to figure out whether this mechanical stress induces only an evaporation of the solvent without altering the 1D structure of the polymer (as this was the case for CP1) (Figure 3), the experimental powder XRD traces of CP3 were compared to the calculated ones of CP4 and CP6 (Figure 7, bottom), two polymers for which no crystallization molecules exist in the lattice even though L2 was used for the synthesis of latter CPs.

The attempt was unsuccessful as there is no resemblance. The conclusion is that CP3 and CP5 are unstable with time, temperature, and vacuum conditions as they lose the solvent meaning these are kinetic products becoming thermodynamic ones because the solvent does not reenter their lattice.

Moreover, when these materials are subjected to increased pressure from crushing, there is an irreversible change of structure (i.e., new thermodynamic product). The latter process could be the result of a combination of both losing the solvent and leaving space for reorganization of the structure. Because the structures of CP3 and CP5 are unknown after subjecting them to these conditions, this possible explanation is still speculative.

**Crystal Transformation of CP3 and CP5.** To determine whether there is transformation for CP3 and CP5, powder of CP3 after MeCN removal was redissolved in MeCN and prismlike crystals similar to those obtained after synthesis were formed. However, the powder XRD measurements confirmed that the pattern of the recovered crystals from the initial powder is not identical to the calculated PXRD pattern. These crystals were only verified by PXRD, which indicated that the molecule is not identical (Figure 6, green line).

Therefore, this speculation of the crystal transformation for CP3 and CP5 upon solvent removal is assumed to be correct because the obtained single crystals after redissolving in MeCN showed also different PXRD patterns from any previous ones (Figure 6).

On the other hand, PXRD patterns for CP2, CP4, and CP6 as synthesized were compared to the calculated PXRD patterns and found to be identical (Figure 7). This clearly indicates that CP2, CP4, and CP6 do not undergo any crystal transformation upon crushing. In addition, the fact that these do not incorporate the solvent in the cavity means that they do not collapse. Therefore, we can conclude that the 1D CPs (CP3,...
and CP5) with MeCN in the voids will not hold the solvent for long as the acetonitrile seems to evaporate upon crushing the crystals.

**CONCLUSIONS**

Ligand design going from L1 to L2 (i.e., PMe3 to PEt3) permitted to generate 1D coordination polymers without any crystallization solvent trapped in the voids. The predictability comes in effect due to the length of alkyl chain on the PEt3 of L2 as compared to L1, which has PMe3. Even though CP3–CP6 are identical as they are all coordinated in the same fashion and are 1D CPs, CP3 and CP5 show crystallization molecules (MeCN in their voids), whereas CP4 and CP6 have no crystallization molecule. This is so because of the crystallization molecules which will occupy the voids available for the polymers made with L1 as there is a short alkyl chain (i.e., PMe3), whereas for the polymers made from L2, no solvent occupies the voids due to steric hindrance of the alkyl chain (i.e., PEt3) and thus resulting in more compact lattice as was slightly heated and allowed to cool at room temperature, thus forming crystals. The solvent was removed as there is no space available for the solvent to be trapped in. This phenomenon is illustrated by the formation of a 2D CP1 when L1 is used, and MeCN is seen trapped in the cavity when L2 forms a 1D CP2 and the cluster step cubane SBU has broken.

**EXPERIMENTAL SECTION**

**Materials.** CuI, CuBr, CuCl, and trans- and cis-dichlorobis-(trimethylphosphine)platinum(II), were purchased from Aldrich. L1 was prepared as previously reported by our group, whereas L2 (see SI) was prepared according to a standard procedure outlined as L1 above and as reported in the literature using 4-ethynylthioanisole, which was synthesized as previously reported.

**Synthesis of [(Cu_{2}I_{2})_n]_L1-MeCN]_n (CP1).** Acetonitrile (5 mL) was bubbled under argon for 20 min. L1 (50 mg, 0.078 mmol) was added, followed by CuI (29.7 mg, 0.16 mmol). The mixture was stirred for 2 h at room temperature. The mixture was slightly heated and then allowed to cool at room temperature, thus forming crystals. The solvent was removed and dried under vacuum. Anal. Calcd for C_{14}H_{19}Cu_{2}I_{2}N_{2}Pt_{0.50}S_{2} (742.76): C, 19.99; H, 2.26; N, 0.49%. Found: C, 20.73; H, 3.27; N, 0.49%. The found elemental analysis in this case is lower due to suspected desolvation of the CP. IR (cm⁻¹): 2978, ν(CH); 2887, ν(CH); 2108, ν(C≡C); 1645, ν(C≡C).

**Synthesis of [(Cu_{2}I_{2})_L2-MeCN]_n (CP2).** Acetonitrile (5 mL) was bubbled under argon for 20 min. L2 (30.0 mg, 0.041 mmol) was added, followed by CuCl (30.7 mg, 0.18 mmol). The mixture was stirred for 2 h at room temperature. The mixture was slightly heated and allowed to cool at room temperature, which facilitates crystal formation. The solvent was removed and dried under vacuum for 1 day. Anal. Calcd for C_{30}H_{44}Cu_{2}I_{2}N_{2}P_{2}Pt_{2}S_{4} (1106.68): C, 32.52; H, 3.98%. Found: C, 32.48; H, 4.42%. IR (cm⁻¹): 2971, ν(CH); 2868, ν(CH); 2107, ν(C≡C); 1663, ν(C≡C).

**Synthesis of [(Cu_{2}Br_{2})_L1-2MeCN]_n (CP3).** Acetonitrile (5 mL) was bubbled under argon for 20 min. L1 (50.0 mg, 0.078 mmol) was added, followed by CuBr (22 mg, 0.16 mmol). The mixture was stirred for 2 h at room temperature. The mixture was slightly heated and allowed to cool at room temperature, facilitating crystal formation. Anal. Calcd for C_{30}H_{44}Br_{2}Cu_{2}N_{2}P_{2}Pt_{2} (1010.65): C, 33.24; H, 3.76; N, 2.77%. Found: C, 31.89; H, 3.63; N, 0.25%. The found elemental analysis in this case is lower due to suspected desolvation of the CP. IR (cm⁻¹): 2968, ν(CH); 2889, ν(CH); 2109, ν(C≡C); 1650, ν(C≡C).

**Synthesis of [(Cu_{2}Br_{2})_L2]_n (CP4).** Acetonitrile (5 mL) was bubbled under argon for 20 min. L2 (30.0 mg, 0.041 mmol) was added, followed by CuBr (11.8 mg, 0.082 mmol). The mixture was stirred for 2 h at room temperature. The mixture was slightly heated and allowed to cool at room temperature, facilitating crystal formation. Anal. Calcd for C_{30}H_{44}Br_{2}Cu_{2}P_{2}Pt_{2}S_{2} (1012.70): C, 35.54; H, 4.34%. Found: C, 35.60; H, 4.31%. IR (cm⁻¹): 2970, ν(CH); 2867, ν(CH); 2107, ν(C≡C); 1661, ν(C≡C).

**Synthesis of [(Cu_{2}Cl_{2})_L1-MeCN]_n (CP5).** Acetonitrile (5 mL) was bubbled under argon for 20 min. L1 (40.0 mg, 0.062 mmol) was added, followed by CuCl (12.3 mg, 0.13 mmol). The mixture was stirred for 2 h at room temperature. The mixture was slightly heated and allowed to cool at room temperature, facilitating crystal formation. Anal. Calcd for C_{30}H_{44}Cl_{2}Cu_{2}N_{2}P_{2}Pt_{0.50}S_{2} (923.78): C, 38.96; H, 4.76%. Found: C, 38.83; H, 4.67%. IR (cm⁻¹): 2970, ν(CH); 2868, ν(CH); 2108, ν(C≡C); 1645, ν(C≡C).

**Synthesis of [(Cu_{2}Cl_{2})_L2]_n (CP6).** Acetonitrile (5 mL) was bubbled under argon for 20 min. L2 (20.0 mg, 0.050 mmol) was added, followed by CuCl (8.9 mg, 0.10 mmol). The mixture was stirred for 2 h at room temperature. The mixture was slightly heated and allowed to cool at room temperature, facilitating crystal formation. Anal. Calcd for C_{30}H_{44}Cl_{2}Cu_{2}P_{2}Pt_{0.50}S_{2} (923.78): C, 38.96; H, 4.76%. Found: C, 38.83; H, 4.67%. IR (cm⁻¹): 2970, ν(CH); 2868, ν(CH); 2108, ν(C≡C); 1645, ν(C≡C).

**Gas Sorption Isotherm Measurements.** Gas sorption isotherms were measured using Micromeritics instrument “Accelerated Surface Area and Porosimetry” (ASAP 2020) analyzer at low pressure ranging between 0 and 1100 mbar (~1.1 bar). Warm and cold free space correction measurements were performed for the isotherms using ultrahigh-purity He gas with purity of 99.9999%. The other gases used are of high grade with purities of 99.999 and 99.99% for N₂ and CO₂ gases, respectively. The measurements were performed at 77 K for N₂ gas, whereas for CO₂ gas, the measurements were performed at 273 K. Before performing the sorption measurements, the samples were heated under reduced pressure of 600 mbar at 110 °C for approximately 6 h and their mass was measured. Then, the samples were backfilled with N₂ and transported to the analysis port where further evacuation was done for 2 h before starting the whole analysis. The surface area and pore volumes were calculated by Brunauer−Emmett−Teller (BET) and density functional theory (DFT) models for N₂ and CO₂, respectively.

**Important notice.** Single crystals were grown from evaporation of acetonitrile solutions. For analyses, such as BET and TGA, the crystals were carefully selected from the dried sample under a microscope. For powder diffraction and luminescence analyses, these crystals were then crushed using a mortar to introduce the powder inside the capillaries.

**Instruments.** Solid-state UV−vis were recorded using a Varian Cary 50 spectrophotometer at 298 K with a grazing-angle transmittance apparatus having a homemade 77 K sample holder. Steady-state fluorescence and excitation spectra were measured on an Edinburgh Instruments FL980 phosphorimeter equipped with single monochromators. All samples were fished out as single crystals under the microscope and were crushed.
prior to use. The steady-state fluorescence spectra were recorded using a capillary. These spectra were corrected for instrument response. The Edinburgh Instruments FL980 phosphorimeter is equipped with a “flash” pulsed lamp. The repetition rate of the pulse can be adjusted from 1 to 100 Hz. The instrument was also used to measure the chromaticity. The TGA traces were acquired on a PerkinElmer TGA 7 apparatus in the temperature range of 20–900 °C at 10 °C/min under an argon atmosphere. The figures were treated by Origin software.

**X-ray Crystallography.** A clear pale yellow prismatic single crystal of L2 was measured on a Bruker Apex DUO system equipped with a Cu Kα ImuS microfocus source with MX optics (λ = 1.54186 Å). Clear light yellow prismatic single crystals of CP1, CP3, and CP6; a clear intense yellow prismatic single crystal of CP2, a clear pale orange prismatic single crystal of CP4, and a clear light orange prismatic single crystal of CP5 were measured on a Bruker Kappa APEX II DUO CCD system equipped with a TRIUMPH curved crystal monochromator and a Mo fine-focus tube (λ = 0.71073 Å). Diffraction data were recorded at 173 K for L2, CP1, CP2, CP3, CP4, CP5, and CP6. A total of 797 frames were collected for L2, CP1, CP2, CP3, CP4, CP5, and CP6. The frames were integrated with the Bruker SAINT software package using a narrow-frame software package using a narrow-frame algorithm for all CPs and a wide-frame algorithm was used for L2. Data were corrected for absorption effects using the multiscan method (SADABS).22 The structures were solved and refined using the Bruker SHELXTL software package using space group P1 with Z = 1 for L2, space group P1 with Z = 2 for CP1, space group P1 with Z = 1 for CP4, CP5, and CP6, space group P121 with Z = 2 for CP2, and space group P1 with Z = 1 for CP3. All nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions and included in final refinement in a riding model with isotropic temperature parameters set to Uiso(H) = 1.5 Ueq(C). Crystal data, data collection, and structure refinement of all compounds are presented in Table S1. Important notice: the crystal structures of CP3 and CP5 undergo a phase change upon crushing. The structure of the resulting materials is not known.

**Powder XRD Measurements.** Each sample of CP1–CP4 and CP6 were mixed with a small amount of Paratone oil and cut to approximately 0.3 × 0.3 × 0.3 mm³. The samples were placed on a sample holder, which was then mounted on a Bruker APEX DUO X-ray diffractometer at 173 K. A total number of six correlated runs per sample were done with φ scan of 360°. Each sample was then exposed to 270 s on the Cu microfocus anode (1.54184 Å) and the CCD APEX II detector at 150 mm distance. The runs were collected from −12 to −72° 2Θ and 6 to 36° ω were treated and integrated with the XSW2 Evalu Bruker software to produce WAXD diffraction patterns from 2.5 to 80° 2Θ. The patterns were treated with Diffrac.Eva version 2.0 from Bruker.

**Procedure for Solvent Removal and Exposure to Solvent Vapor.** A small amount of polymers CP1, CP3, and CP5 were inserted in small vials, and the crystallization molecules were removed by heating under reduced pressure (600 mbar) up to 110 °C for 6 h. The removal of the crystallization molecules was confirmed with TGA measurements. The samples treated in this manner were also inserted in small vials, which were then placed in a desiccator containing solvent (MeCN) in a larger recipient. These vials were exposed under reduced pressure (500 mbar) at room temperature for 2 days. For CP1, the reintroduction of the solvent was possible, at least in part, but this was not the case for CP3 and CP5.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01352.

Crystallographic data in CIF format are provided for both L2 and CP1–CP6 (CIF) (CIF) (CIF) (CIF) (CIF) (CIF) (CIF). Summary of X-ray data collection and refinement of L2 and CP1–CP6. TGA of L2 and CP1–CP6, Raman spectra of L1, CP1, CP3, and CP5. Ball and stick representation of CP2–CP6 and powder XRD of CP5 (PDF).

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**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC), the Fonds de recherche du Québec-Nature et technologies (FRQNT), and the Centre Québécois des Matériaux Fonctionnels (CQMF).

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