Electronic and vibrational analysis of porphyrazine liquid-crystalline structure: Toward photochemical phase switching

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Dedicated to Edward Solomon.

Abstract

The electronic and vibrational Raman spectra of octa-substituted (R = –SC_{10}H_{21}) Co- and Cu-porphyrazines are reported in their solid-state, mesophase, and isotropic liquid forms, as well as in THF solution. Their electronic spectra are composed of traditional Soret (CuS_{10} = 355 nm, CoS_{10} = 347 nm) and lower energy Q-bands (CuS_{10} = 669 nm, CoS_{10} = 639 nm), as well as a weaker, functionality-specific sulfur n\_porphyrin \pi^* feature (CuS_{10} = 500 nm; CoS_{10} = 447 nm). In contrast to the broad Q-band for CoS_{10} in all three neat phases, the lower energy analogue for CuS_{10} is markedly sharper in the microcrystalline state, but similarly broadens in the mesophase, indicative of long range macrocycle \pi-\pi interactions that persist even into the liquid state. The resonance (\lambda = 647 nm) and off-resonance (\lambda = 785 nm) Raman spectra of these materials in each phase exhibit four diagnostic vibrations; the C_{\alpha}-N_{m} stretch (1540–1553 cm\^{-1}), C_{\beta}-C_{\beta} stretch (1450 cm\^{-1}), C_{\alpha}-C_{\beta}-N_{p} stretch (1300–1315 cm\^{-1}), and C_{\alpha}-C_{\beta} stretch (1070 cm\^{-1}). For CoS_{10}, these vibrations systematically shift to lower energy upon melting, while those for CuS_{10} collapse to degenerate sets. The differences in the electronic and vibrational profiles as a function of temperature suggest that the mesophase structure is governed by strong axial Co–S interactions for CoS_{10} which template macrocycle \pi-\pi stacking, while for CuS_{10} the same contacts exist, but they are phase dependent and markedly weaker. These inter-porphyrazine interactions are, therefore, responsible for the distinct differences in the melting and clearing temperatures of their respective mesophases. Finally, based on these diagnostic spectroscopic signatures, a photo-thermal, phase-switching mechanism is demonstrated with \lambda = 785 nm excitation at reduced temperatures, leading to the ability to spectrally monitor and phase change with a single photon source.

Keywords: Liquid crystal; Porphyrazines; Raman spectroscopy; Electronic absorption of liquid crystals

1. Introduction

The ability to generate a fluid, yet self-assembled, organized structure over long range with optical, magnetic, or conductive response have made liquid crystals (LC) an extremely valuable material for microelectronic devices such as electroluminescent displays of high uniformity [1], thermally-tunable semi-conductors [2,3], and thin-film optical photo-conductors [4–7]. The convergence of enhanced single molecule properties with controllable intermolecular interactions via hybrid synthetic approaches has led to the development of selective materials that pervade applied electronics, most notably, organic rigid rod (calamitic) LCs that align in an electric field for technologically ubiquitous twisted nematic LC displays [8–11].

One of the challenges associated with control of LC behavior is the development of anisotropic, nanoscale segregation within a specific dimension [12]. To this end, discotic liquid crystalline materials that form columnar phases exhibit specific dimensionality and have found utility in self-ordering, micro-electronic components capable of behaving as uni-dimensional conductors/photo-conductors [7]. The typical molecular motif of these compounds

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consists of an aromatic core which has been peripherally functionalized with long alkyl chains, resulting in columnar mesophases with core aromatic domains capable of behaving as charge carriers, surrounded by insulating alkyl chains that restrict charge transport to the columnar axis [13]. Although the conductivity and luminescent properties of organic LCs (e.g. discotics) is remarkable, by virtue of their closed-shell electronic structure, these materials are diamagnetic and require high external magnetic fields (~5 T) [1] to generate monodomains in which all mesophase columns are aligned over long range. Incorporation of open-shell metal ions into nanoscale-segregated, discotic architectures hybridizes the traditional mesomorphic character of discotics with tunable paramagnetism in both magnitude and directionality. This introduces the potential for facile magnetic alignment and switchable response at more modest external fields [14]. More broadly, metal ion incorporation into LC frameworks to form metallomesogens can also engender metal-mediated, chimeric electronic incorporation into LC frameworks to form metallomesogens via disparate intermolecular interactions [19–21], while specific frequency shifts in the vibrational features are diagnostic of the intermolecular interactions responsible for phase change [22–24]. These spectroscopic signatures are then correlated to explain the marked differences in the clearing points of CoS10 and CuS10. Finally, the intense electronic transitions exhibited by these materials afford an opportunity for introduction of thermal energy into liquid crystalline domains via photo-thermal heating, which permits remote phase switching of these materials while simultaneously monitoring these transitions via vibrational analysis.

2. Experimental

2.1. Sample preparation

Metalloporphyrazines were prepared according to methods previously described [14,18,25,26]. Sample integrities were confirmed by LDI- and FAB-MS, and elemental analysis.

2.2. Electronic absorption spectroscopy

Solution and neat electronic absorption spectra were obtained using a Perkin-Elmer Lambda 19 UV–Vis–NIR spectrometer. All solution data were recorded at ambient temperature. Neat samples were prepared via deposition of a drop (~5 mm) of a concentrated toluene solution of the sample on a quartz window. Solvent was allowed to evaporate at room temperature for a minimum of 30 min. prior to mounting in a copper cell for spectral analysis. Thermal excitation was performed by a 90 W heating element mounted within a 5° × 1° copper cylinder in contact with the copper sample cell. Temperature was controlled using a Set-Temp Digital temperature controller (Laboratory Devices Inc.) with a K-type thermocouple mounted to the copper sample holder. Samples were heated to specific temperatures and allowed to equilibrate for approximately 5 min. prior to collection of spectra.

2.3. Raman spectroscopy

Off-resonance Raman spectra and images of samples were recorded using a Renishaw 1000B micro-Raman spectrometer equipped with a 785 nm SDL diode laser under variable power (0.2–20 mW) conditions. Temperature-dependent Raman spectra were obtained using a Linkam model TDS 600 variable temperature hot-state/cold-stage
Resonance Raman spectra were collected using $\lambda = 647.5$ nm laser excitation from a Coherent Innova 300 Kr$^+$ ion laser. Backscattered light (\sim 35$^\circ$) was collected using a Nikon Nikkor AI-S 85 mm (f/1.4) camera lens and was focused through a depolarizer (CVI) onto the entrance slit of a custom-built, f/4 subtractive-mode, double monochromator equipped with 600 grooves/mm (500 nm blaze) gratings. Output of this filter stage was focused on the entrance slit of an Acton Spectrapro 500i spectrometer (f/6.5) operating with a 1200 grooves/mm (750 nm blaze) grating. The dispersed scattering was recorded using a back-illuminated, liquid N$_2$ cooled charge coupled device (Princeton Instruments) with a 30 mm $\times$ 14.4 mm active area (2500 $\times$ 600 pixel array). Solution spectra were measured in spinning, thin-walled, 5 mm glass NMR tubes. Neat spectra were collected by depositing powdered samples on the surface of a quartz window backed by a copper slug mounted in the custom heating element used for variable temperature electronic spectroscopy.

2.4. Computational methods and vibrational analysis

To understand the electronic structures of the different species, computational studies were performed using density functional theory with the standard B3LYP hybrid functional. We utilized the 6-31+G(d,p) basis set (containing a set of spd diffuse functions along with f-polarization functions) on Co and Cu, and the 6-31G(d,p) basis set (containing d-type polarization functions on C, N, and S, and p-polarization functions on H) to optimize the molecular geometries and to obtain the harmonic vibrational frequencies and the associated Raman intensities. Both structures minimize in $C_4$ symmetry with alternating methyl groups located above and below the molecular plane. The calculated vibrational frequencies (gas phase) were scaled uniformly by a factor of 0.982, and resulted in very good overall agreement between the computed and experimental ($\lambda_{\text{exc}} = 785$ nm, THF solution) values. All calculations were performed with the Gaussian-03 [27] program suite.

3. Results and discussion

3.1. Electronic discussion

The solution electronic absorption spectra of CuS10 and CoS10 (Fig. 1a) are dominated by two distinct transitions typical of metalloporphyrin architecture [28,29]: a high energy Soret band (CuS10 = 355 nm, CoS10 = 347 nm) and a low energy Q-band (CuS10 = 669 nm, CoS10 = 639 nm) showing a vibronic overtone to higher energy ($\nu \sim 1250$ cm$^{-1}$) [29]. An additional feature arising from a $n$sulfur $\rightarrow \pi^*$ transition is apparent at $\lambda \sim 500$ nm for CuS10 and 447 nm for CoS10, which is in general agreement with the electronic absorption spectra reported for MS1 compounds [19,25,26]. The blue-shift of the CoS10 spectral features relative to CuS10 is common to other metallo-porphyrin and porphyrine frameworks, and is related to the relative hardness of the central ion [29].

For CoS10 in the solid state (Fig. 1b), this general electronic structure is retained, though substantial broadening of the Q-band from a full-width, half-max (FWHM) of $\sim 1200$ cm$^{-1}$ in solution to $\sim 4000$ cm$^{-1}$ in the solid state, and a red-shift from of $\lambda = 639$ nm (solution) to 690 nm (solid) are observed ($\Delta \sim 1150$ cm$^{-1}$). Both the broadening [19,21] and red-shift [20] can be attributed to increased $\pi$-stacking of the porphyrine macrocycles that manifests
over long range. Heating neat CoS10 to its mesophase (100 °C) results in a slight blue-shift of the Q- (19 nm) and Soret bands (6 nm), but no significant changes in the linewidths are observed. Similarly, when CoS10 is heated past the clearing point, the Q- and Soret bands further blue-shift (6 and 10 nm, respectively) while maintaining their linewidths. This indicates that the intermolecular structure for CoS10 is maintained in all three phases, but the degree of π-stacking is systematically relaxed, as evidenced by the blue-shift of the Q and Soret bands.

In contrast, the neat electronic absorption spectrum of CuS10 demonstrates distinct differences in macroscopic structure upon transition from crystalline to mesophase and isotropic liquid (Fig. 1c). Unlike CoS10, the solid-state absorption profile of CuS10 retains the general characteristics of the solution spectrum with respect to the Soret and Q transitions, but the Q-band shows substantial variability between these spectra. As a solid, the Q-band red-shifts to λ = 726 nm (∆ = 1170 cm⁻¹) relative to THF solution, but unlike CoS10, CuS10 maintains a narrow bandwidth (FWHM ~1100 cm⁻¹). The shift to lower energy can be readily explained by intermolecular π-interactions between macrocycles as shown for crystallographically characterized Cu-thiadiazole porphyrazines, which exhibit a 3.2 Å inter-planar separation [30]. The lack of significant broadening of the Q-band despite the presence of π-interactions may be related to a lower degree of long-range π-stacking in the solid. Of note is the sharpness of the low-energy side of the Q-band relative to the broadened, high-energy slope, indicating the presence of an unresolved vibrational component of the Q-band underlying the solid-state spectrum. A higher energy transition is also apparent at λ = 624 nm, which is not directly observed in solution. This feature has been reported previously [31], however a thorough discussion of the assignment has not been presented. Our results suggest that the origin of the λ = 624 nm band may derive from small, asymmetric molecular distortion upon crystallization, introducing distinct Qₓ and Qᵧ transitions which are reminiscent of those observed for free-base thioalkyl porphyrazines [19,32–35]. The π-nature of the transition is consistent with resonance Raman enhancement of core macrocycle ring modes upon λ = 647 nm excitation. Additionally, in contrast to the ~1250 cm⁻¹ energy gap between the parent and vibrational component of Q-band, which derives from a combination of macrocycle ring modes [29], the separation of the Qₓ and Qᵧ symmetry partners is typically greater, on the order of 3000 cm⁻¹. The observed 2250 cm⁻¹ separation of the Q-bands for crystalline CuS10 is significantly larger than expected for the vibrational components of a Q-band, and thus may derive from a decrease in molecular symmetry upon crystallization.

Upon heating to the mesophase, the Q-band broadens significantly (FWHM ~3300 cm⁻¹) and shows a pronounced blue-shift to λ = 686 nm (∆ = 800 cm⁻¹), which encompasses the previously resolved higher energy feature. Since the mesophase allows in-plane rotation of the porphyrazine macrocycle within the liquid crystal columnar order, averaging of Qₓ and Qᵧ asymmetry occurs upon melting, and the spectra now exhibit extended π-stacking as observed for CoS10. Heating past the clearing point does not further change the shape or energy of the electronic transitions in CuS10. Therefore, the mesophase and isotropic electronic absorption spectra of CuS10 reveal extended order consistent with that observed for CoS10 throughout its phases. The clear blue-shift upon melting indicates that the crystal packing responsible for the change in electronic structure of solid CuS10 has been relaxed in the higher temperature phases. Thus, though disparate crystal packing energies are predicted to be responsible for the observed initial melting points of CoS10 and CuS10, the predominant intermolecular forces present in the mesophases of each system should be similar, indicating that the differences in observed clearing points must be, in general, the result of weaker inter-macrocycle interactions within CuS10 mesophase columns relative to CoS10.

It has been shown that substitution of the central metal ion of porphyrazines can have a strong influence on the crystal packing scheme of otherwise identical macrocycles [30]. Indeed, powder diffraction studies of CoS10 and CuS10 reveal that they exhibit different space groups in the solid-state, though detailed structural information is not available due to extensive disordering in the microcrystalline samples examined [14]. For analogous octakis(ethylthio)-porphyrazines (MS2), the observed crystal packing for CoS2 exhibits a herringbone pattern dictated by sulfur lone-pair donation to the half-occupied d(3z²) orbital of the central cobalt ion of an adjacent macrocycle [36]. It is of note that the meso-nitrogen shows no distortion from the macrocycle plane in this X-ray structure, indicating that M-S bonding directs the lone pair parallel to the adjacent macrocycle where it has little interaction with the neighboring π-system. Unfortunately, no crystallographically characterized copper thioalkyl porphyrazines exist for comparison. However, it is apparent based on the distinct electronic absorption features for crystalline CuS10 that this crystal packing motif may not be translated upon substitution of the central metal ion. For crystalline CuS10, the additional electron density in the d(3z²) orbital would be expected to lead to a Jahn–Teller distorted, filled-filled axial interaction in pure C₄ symmetry with one of the sulfur lone pairs in the solid-state structure, leading to no axial interaction and only weak intermolecular association.

For structurally characterized metallo-thiadiazole porphyrazines containing metal ions that strongly bind axial ligands (e.g. Co³⁺, Zn²⁺, and Fe²⁺), crystal packing is typically dictated by axial interactions with lone pairs from thiadiazole nitrogen atoms of adjacent macrocycles [30]. Conversely, for copper thiadiazole porphyrazines, the Jahn–Teller distortion and the accompanying lack of, or elongation of, axial bonds results in a crystalline structure in which π-π interactions are maximized at the expense of axial association. The resulting macroscopic structure reveals porphyrazine units that typically pack with meso-
nitrogen atoms from adjacent molecules non-covalently capping the central copper ion [30]. In the case of CuS10, the presence of sp³ sulfur lone pairs from the periphery side-chains may lead to an additional weak-axial interaction with the Cu-center upon transition to the mesophase, in which sulfur coordination causes the macrocycle π-π interactions to slip slightly as is the case for CoS10. This hypothesis is consistent with the observation that all MS10 metalloporphyrazines highlighted above exhibit a mesophase, but the free-base derivative does not. The weaker axial interaction for CuS10 vs. CoS10 is also manifested in the more pronounced blue-shift of the Q-band in the mesophase and isotropic liquid states.

### 3.2. Vibrational analysis

A comparison between the resonance Raman spectra of the solution, crystalline, meso- and isotropic phases of CoS10 and CuS10 (Fig. 2) shows distinct changes in both the energy and asymmetry of several molecular vibrations upon solvation and melting. Subsequent heating of these metalloporphyrazines past their clearing temperatures shows no additional spectral change of significance. The resonance Raman spectra of CoS10 exhibit systematic vibrational shifts to lower energy upon phase change, whereas the spectra of CuS10 simplify upon melting as sets of vibrations collapse to form fewer distinct signatures due to increased molecular symmetry and averaging. Most notable are the modes in both at ~1075, ~1300, ~1450, and ~1540 cm⁻¹. Although a normal mode analysis of the vibrational structure of assorted porphyrazines and phthalocyanines has been performed [37–40], a specific investigation of thioalkyl porphyrazines has not been previously reported. Since the vibrational structure of a porphyrazine will be perturbed by the addition of electron rich sulfur to the periphery of the macrocycle through mixing of the sulfur lone pairs into the π-system, we have undertaken a computational analysis of the vibrational structure of CoS10 and CuS10. To minimize computational time, MS10 molecules were modeled as MS1, preserving the core macrocycle structure and influence of the thioalkyl groups while minimizing the difficulties of reaching a geometric minimum for flexible –C₁₀H₂₁ n-decyl chains. Though the alkyl chains of the thioalkylporphyrazines have a strong influence on their liquid crystalline behavior [18,19,41], the vibrational structures of these compounds are dominated by in-plane macrocycle distortions, allowing our model to accurately elucidate the specific normal modes associated with the observed vibrations.

Comparison of calculated MS1 and measured MS10 Raman spectra (Table 1) show good agreement for both CoS10 and CuS10. The solution spectra correlate within 21 cm⁻¹ for all predominant vibrations; the only exception is the Cα–Nₘᵢ stretch which exhibits a substantially greater deviation (ΔCoS10 = 50 cm⁻¹, ΔCuS10 = 35 cm⁻¹) from the gas phase computation. This is not surprising since the exposed meso-nitrogen lone pair is sensitive to the external chemical environment, and may serve as a reporter of periphery structure intrusion. Between CoS10 and CuS10, the intensity and energy of many observed solution vibrations are different, but there is a high degree of conservation of the Cα–Nₘᵢ, Cβ–C₈, C₈–C₉–Nₘᵢ, and Cα–C₈ stretches (Fig. 3), which are the most diagnostic of phase change.

The Cα–Nₘᵢ stretches at 1552 cm⁻¹ for crystalline CoS10 and 1543 cm⁻¹ for CuS10 (Fig. 2) show a disparate but discernible shift to lower energy upon solvation in THF (ΔCoS10 = 10 cm⁻¹, ΔCuS10 = 3 cm⁻¹), which is expected since the exposed lone pair of the meso-nitrogens should be quite sensitive to molecular environment. A similar shift occurs for neat CoS10 upon melting from the solid to the mesophase (100 °C), with no additional energy change observed upon heating past the clearing point. Conversely, for neat CuS10, the Cα–Nₘᵢ vibration shows little shift in energy upon heating through the mesophase or past the clearing point.

For the CoS10 Cβ–C₈ stretch (ν = 1453 cm⁻¹), shifts comparable to those described for Cα–Nₘᵢ are observed; once again, the energy of the vibration is decreased upon solvation and melting. Since it is expected that the sulfur adjacent to the β-carbon directs the crystal packing of

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**Fig. 2.** Resonance Raman spectra (λₑₓ㎝ = 647.5 nm) of THF solution (RT), solid, meso- and isotropic phases of: (a) CoS10 and (b) CuS10. Temperatures are given in °C.
<table>
<thead>
<tr>
<th>Assignment</th>
<th>Calculated symmetry</th>
<th>CoS1 (Calc. cm(^{-1}))</th>
<th>CoS10 (Calc. cm(^{-1}))</th>
<th>Diff.</th>
<th>CuS1 (Calc. cm(^{-1}))</th>
<th>CuS10 (Calc. cm(^{-1}))</th>
<th>Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_\alpha)–N(_m) stretch</td>
<td>B</td>
<td>1592</td>
<td>1542</td>
<td>50</td>
<td>1578</td>
<td>1543</td>
<td>35</td>
</tr>
<tr>
<td>C(<em>\alpha)–N(<em>m)/C(</em>\beta)–C(</em>\beta) stretch</td>
<td>A</td>
<td>1529</td>
<td></td>
<td></td>
<td>1516</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_\alpha)–N(<em>m)–C(</em>\alpha) stretch</td>
<td>A</td>
<td>1512</td>
<td>1505</td>
<td>7</td>
<td>1491</td>
<td>1512</td>
<td>21</td>
</tr>
<tr>
<td>C(<em>\beta)–C(</em>\beta) stretch</td>
<td>A</td>
<td>1474</td>
<td></td>
<td></td>
<td>1461</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(<em>\beta)–C(</em>\beta) stretch</td>
<td>B</td>
<td>1465</td>
<td>1453</td>
<td>12</td>
<td>1458</td>
<td>1452</td>
<td>6</td>
</tr>
<tr>
<td>C(<em>\alpha)–N(<em>m)–C(</em>\alpha) bend/C(</em>\alpha)–N(<em>p)–C(</em>\alpha) bend</td>
<td>A</td>
<td>1396</td>
<td>1395</td>
<td>1</td>
<td>1392</td>
<td>1382</td>
<td>10</td>
</tr>
<tr>
<td>C(<em>\beta)–C(</em>\beta)–N(_\alpha) stretch</td>
<td>B</td>
<td>1316</td>
<td>1301</td>
<td>15</td>
<td>1300</td>
<td>1315</td>
<td>15</td>
</tr>
<tr>
<td>Pyrrole breathing</td>
<td>B</td>
<td>1109</td>
<td>1100</td>
<td>9</td>
<td>1110</td>
<td>1107</td>
<td>3</td>
</tr>
<tr>
<td>C(<em>\alpha)–C(</em>\beta) stretch</td>
<td>B</td>
<td>1083</td>
<td>1076</td>
<td>7</td>
<td>1081</td>
<td>1070</td>
<td>11</td>
</tr>
<tr>
<td>C–H(_3) tilt</td>
<td>B</td>
<td>989</td>
<td></td>
<td></td>
<td>989</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_\alpha)–N(<em>p)–C(</em>\alpha) bend</td>
<td>B</td>
<td>931</td>
<td>935</td>
<td>–4</td>
<td>923</td>
<td>940</td>
<td>–17</td>
</tr>
<tr>
<td>C(_\alpha)–N(<em>p)–C(</em>\alpha) rock</td>
<td>B</td>
<td>760</td>
<td>757</td>
<td>3</td>
<td>754</td>
<td>759</td>
<td>–5</td>
</tr>
<tr>
<td>S–CH(_3) stretch</td>
<td>E</td>
<td>680</td>
<td></td>
<td></td>
<td>680</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Macrocycle breathing</td>
<td>A</td>
<td>587</td>
<td>598</td>
<td>–11</td>
<td>584</td>
<td>600</td>
<td>–14</td>
</tr>
</tbody>
</table>

Fig. 3. Calculated molecular vibrations for CoS1 (C\(_4\) symmetry): (a) C\(_\alpha\)–N\(_m\) stretch (1592 cm\(^{-1}\)), (b) C\(_\beta\)–C\(_\beta\) stretch (1465 cm\(^{-1}\)), (c) C\(_\alpha\)–N\(_p\)–C\(_\alpha\) stretch (1316 cm\(^{-1}\)), and (d) C\(_\alpha\)–C\(_\beta\) stretch (1083 cm\(^{-1}\)).
Off resonance ($\lambda_{\text{exc}} = 785$ nm) Raman spectra taken in 10°C increments with emphasis on the C–N, C–C, and C–C–N vibrations more clearly show these trends (Fig. 4). Once again, the Raman spectra indicate that the primary vibrations of CoS10 shift to lower energy upon warming, whereas the features observed for crystalline CuS10 exhibit multiple signatures for the same in-plane normal mode that collapse upon phase change. Consistent with this observation, the computed vibrational profile reveals two nearly degenerate C–C vibrations which are not resolved in the $\lambda = 785$ nm solution spectrum, but due to crystal packing effects, are individually detected for multiple C–C sites in the solid-state Raman profile. Apparent in both the CoS10 and CuS10 off-resonance Raman spectra are phase changes at temperatures ($-30$ to $-10$ °C for CoS10 and $40$ to $60$ °C for CuS10) lower than expected based the established melting points of these materials due to laser-induced, photo-thermal heating of the samples. For the temperatures through which melting occurs, the observed spectra are an addition of the crystalline and mesophase profiles arising from incomplete melting due to the non-uniform laser beam profile over the photolyzed area resulting in uneven heating of the sample. For CoS10, the appearance of spectral features correlating to the mesophase begins at $-30$ °C, with complete phase change apparent by $-10$ °C. This can be seen clearly for the C–N vibration in which a low energy shoulder from the mesophase CoS10 begins to emerge at $-30$ °C, finally dominating and remaining unchanged at $-10$ °C. For CuS10, the multiplicity of the C–C and C–C–N stretches in crystalline CuS10 are preserved through the heating ramp up to $30$ °C, past which broadening is apparent ($40$–$60$ °C) and finally, a single isotropic feature is observed. The lower laser-induced phase transition temperature for CoS10 relative to CuS10 is not a chemical phenomenon, but rather derives from the difference in laser excitation power density used for collection of each data set (CoS10: 1.9 mW; CuS10: 0.19 mW).

3.3. Proposed structures

Based on the electronic and vibrational data, and in conjunction with structurally characterized metalloporphyrines, we propose the models for CoS10 and CuS10 inter-macrocycle interactions in the solid state illustrated in Fig. 5. For CoS10, a crystalline structure strongly directed by the preservation of axial Co–S interactions is consistent with the observed preference for cobalt metalloporphyrines to crystallize in order to maximize axial Co–S bonding with available lone pairs of adjacent molecules [30,36]. Furthermore, this crystalline orientation forces π overlap between adjacent molecules, which is reflected in minimal perturbation of the electronic structure between solid, mesophase, and isotropic liquid states. The physical picture is also supported by Raman data in which crystalline CoS10 exhibits shifts for the C–C vibration consistent with sulfur interactions between adjacent porphyrine units which are maintained, but relaxed upon melting. The shift to lower energy of the C–N vibration in the mesophase and isotropic liquid mandates that the CoS2 meso-nitrogen in the crystalline state is not effectively
interacting with protons from side-chains on the adjacent macrocycles due to their Co–S mediated ring displacement. This restriction is relieved upon transition to the mesophase, which permits free rotation of the macrocycles within the columns. The enhanced degrees of freedom allow the side-chains to sample the void above/below the meso-nitrogen of the adjacent macrocycle leading to weak H-bonding with the C–H bond of the side-chain (Fig. 6a). Dynamic, inter-columnar breathing enhances this effect in the mesophase resulting in the marked shift to lower energy of the C\textsubscript{a}–N\textsubscript{m} vibration analogous to solvation effects by THF.

In contrast, we propose that the order of CuS\textsubscript{10} in the crystalline state is dictated by maximizing overlap between adjacent π-frameworks. Copper metalloporphyrinoids generally do not mediate strong axial bonding interactions in the solid state, and are instead observed to crystallize in motifs that maximize facial π interactions between macrocycles [30]. Extension of this crystal would produce two distinct molecular axes due to the asymmetric distortion of the macrocyclic π system, which is evident in the electronic absorption spectrum of the microcrystalline material. Similarly, the strong π overlap will generate disparate energies for the pyrrole-centered vibrations, as observed in the crystalline Raman spectra for CuS\textsubscript{10}. Such a structure also places the thioalkyl chains in position to fill the void adjacent to the meso-nitrogen of the partner macrocycle, effectively solvating the lone-pair and leading to minimal shift in the C\textsubscript{a}–N\textsubscript{m} vibration across the phases relative to THF solution (Fig. 6b). Upon melting, relaxation of this π overlap will relieve the distorted C\textsubscript{p}–C\textsubscript{N} and C\textsubscript{p}–C\textsubscript{a}–N\textsubscript{p} vibrational components making them nearly degenerate, and leading to a blue-shift of the Q-band as observed in Raman and electronic spectra, respectively, of CuS\textsubscript{10} in the mesophase and isotropic liquid. The accompanying broadening of the electronic spectrum, and its similarity to that of
CoS10 in these phases, suggests that CuS10 must adopt a weak but definable Cu–S interaction upon melting that leads to long range order and liquid crystallinity. Thus, the stronger axial interaction for CoS10 ultimately gives rise to a higher clearing temperature and broader mesophase relative to CuS10.

3.4. Photo-induced switching

To explore the photo-induced phase-switching potential of these liquid crystalline structures, a series of CuS10 spectra were collected at room temperature using incrementally increasing excitation powers (Fig. 7). Photolysis at low laser power (0.2 mW/60 s exposure) generates the typical Raman vibrational profile with no indication of phase change in the sample either through visual microscopic inspection or shifts in vibrational energies. Increasing the laser power to 2 mW leads to immediate broadening of the spectral features and minor frequency shifts indicative of the onset of melting to the mesophase, along with subtle visual changes in phase at the very center of the sample photolysis area. Due to the larger illumination area, the Raman spectral profile is a mixture of solid-state and mesophase vibrational features. Upon increasing the laser power to 5 mW, melting is visually detectable, and is accompanied by complete transformation of the spectrum to that observed for mesophase CuS10 (c.f. Fig. 4b). Further photolysis at higher powers (10, 20 mW) produces only small additional perturbations in the observed spectra at 600 and 1315 cm$^{-1}$, as well as between 1050 and 1100 cm$^{-1}$.

However, images of the sample reveal a more prominent change in sample phase as evidenced by the larger melt area. At 10 mW, the center of image begins to show transition to the isotropic liquid, while the perimeter of the melt area remains liquid crystalline in nature based on the strong similarity of the 5 and 10 mW Raman profiles. At an excitation power of 20 mW, the entire area being sampled converts to the isotropic liquid, and the corresponding Raman spectra reflect the transition by slight spectral sharpening of the bands at 600, 1070, and 1315 cm$^{-1}$. This power dependence of phase, accompanied by a diagnostic spectral signature, suggests a potential utility for metalloporphyrazine liquid crystals in optical, phase-switching applications.

4. Conclusion

Electronic and Raman spectra of CoS10 and CuS10 porphyrazines in solid, mesophase, isotropic liquid, and THF solution reveal $\pi-\pi$ inter-macrocycle interactions that in the mesophase and isotropic liquid are influenced by axial metal interactions with the sulfur of an adjacent macrocycle. For CoS10, these interactions are considerably stronger than for CuS10, as evidenced by the enhanced blue-shift in the electronic spectra for the latter in the mesophase. Accompanying the stacking is a disparate solvation of the meso-nitrogen derived from the alkyl side-chain filling the void and hydrogen bonding with the in-plane sp$^2$ lone pair. The orientation of the $\pi$-stacked macrocycles for CoS10 do not allow this to occur in the solid state, but rather require dynamic ring and chain motion in the mesophase to relieve the restriction. In contrast, for CuS10, we propose that this hydrogen bonding occurs in the solid-state and is maintained through the phases, explaining the lack of a prominent shift in the C=C-N$_m$ vibration. Finally, the ability of the large porphyrazine chromophore to non-radiatively decay optical energy to heat permits photo-thermal phase switching of these materials. In this way, a single laser source can be used to both stimulate and monitor vibrational signatures of each phase via in situ Raman. Methodology of this type may prove useful for the fundamental development of photo- or magneto-optical materials.

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References