# Room Temperature Liquid Porphyrins

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The syntheses of 5,10,15,20-tetrakis(3,4,5-trialkoxyphenyl)porphyrins, which exhibit fluid state behavior at room temperature, are reported. The thermal and rheological measurements indicate that they behave like liquid at 25 °C (298 K).

Porphyrin derivatives are widely applied in functional electronic materials such as sensors,[1a] organic electroluminescent materials,[1b] organic transistors,[1c,1d] solar cells,[1c,1e] nonlinear optics,[1f] and liquid crystals.[1g] π-Expanded porphyrins are used in organic electronic applications due to their large π-conjugation.[1g,2] Porphyrins are also used with functional carbon molecules such as fullerene dyads[3a] and carbon nanotubes (CNTs) for organic electronics.[3b] Although porphyrins are useful for electronic applications, their low solubility in organic solvents makes their handling difficult in solution-process techniques such as spin-coating and printing for device fabrications. Only a few reports are available that describe the use of simple-modified porphyrins with high solubility in organic solvents, and these use polymers. One simple method for increasing porphyrin solubility is introducing long alkyl chains with porphyrins,[1c] incorporating these within polymers, and using sol–gel technique.[4] Liquids are for easy handling and processing. Furthermore, bucky-gels,[5] developed from ionic liquid and CNTs, and liquid fullerenes[6] are reported to be easily processed, and therefore can be used for electronic applications. During our research on simple-modified solution-processible porphyrins, we believed that room temperature (RT) liquid porphyrins might be obtained by an appropriate molecular design. Here, we report the syntheses, thermal properties, and rheological properties of liquid porphyrins at RT. They are single-component molecules with fluidity, which may have potential use in organic electronic applications such as organic solar cells and organic electrochemical cells.

The most general porphyrins are 5,10,15,20-tetraphenylporphyrin (TPP), which are synthesized from pyrrole with benzaldehyde using Lewis acids as catalysts following oxidation with an oxidant such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ).[7] The benzaldehyde units are easily modified by introducing alkyl chains[6] connecting the dendrons to dendrimers,[8] therefore we chose TPP. For our molecular design, to introduce more alkyl chains, prevent stereoisomers, and because we expect the molecule to interact with fullerenes and CNTs, we elected to synthesize 5,10,15,20-tetrakis(3,4,5-trialkoxyphenyl)porphyrins (**1-C$_n$**), in which *n* denotes alkyl chain length (Figure 1). **1-C$_n$** molecules were synthesized as shown in Scheme 1. 3,4,5-Trialkoxybenzaldehydes were synthesized according to a modification of a previously reported procedure.[9] Ethyl 3,4,5-trihydroxybenzoate (**2**) reacted with alkyl bromide and potassium carbonate in DMF at 90 °C to give ethyl 3,4,5-trialkoxybenzoate **3**. **3** was reduced with lithium aluminum
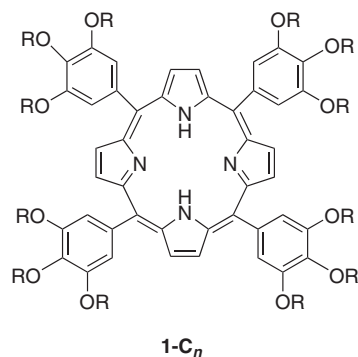
Figure 1. Structure for porphyrins. R and *n* denote *n*-alkyl group and alkyl chain length, respectively.
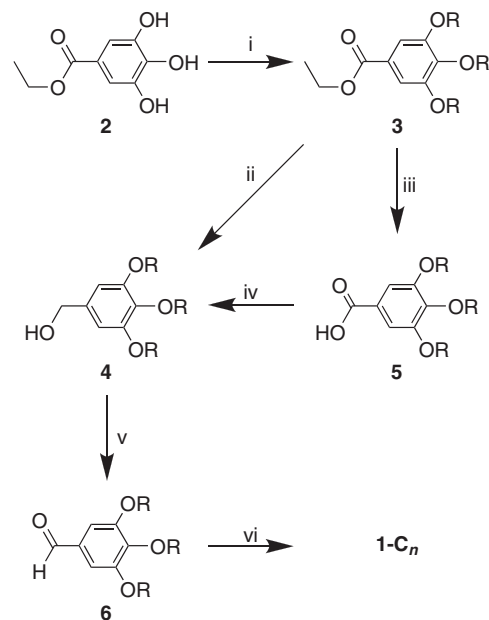
Scheme 1. *Reagents and conditions*: i) alkyl bromide, K$_2$CO$_3$, DMF, 90 °C; ii) LAH, THF, reflux; iii) KOH, THF–MeOH–water, reflux; iv) LAH, THF, reflux; v) MnO$_2$, CHCl$_3$, rt; vi) pyrrole, TFA, CHCl$_3$, rt, then DDQ.

hydride (LAH) in refluxing THF to give 3,4,5-trialkoxybenzylalcohol **4**. In this case, it seemed that the reaction resulted in little decomposition and low yields when the preliminary material was oil. To prevent decomposition, the reduction processes were performed in two steps: first, deprotection of ester refluxing in THF–methanol–water with potassium hydroxide gave 3,4,5-trialkoxybenzoic acid **5**, following the reaction

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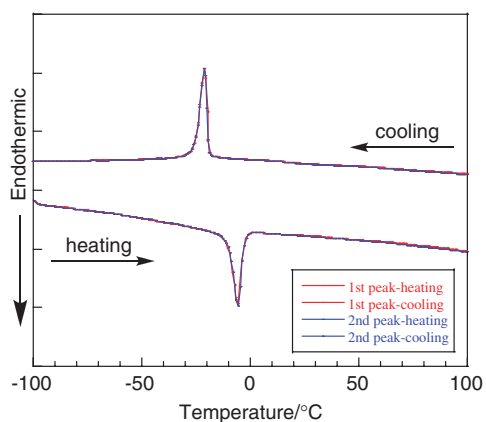
Figure 2. DSC chart of **1-C₁₂** at a heating and cooling rate of $10\,°C\,min^{-1}$ under nitrogen: 1st scan (red line) and 2nd scan (blue line), respectively.

Figure 3. Rheological behavior of **1-C₁₂** at 25 °C. Angular frequency dependence on storage and loss moduli at a γ of 10, 100, and 1000.

with LAH in refluxing THF to give **4**. **4** was reacted with manganese(IV) oxide in chloroform at RT to give 3,4,5-trialkoxybenzaldehyde **6**. **1-C$_n$**s were obtained by a reaction with pyrrole and **6** in chloroform using trifluoroacetic acid (TFA) as a catalyst at RT followed by oxidation with DDQ.[7] The structures of **1-C$_n$** molecules were assigned by ^1H NMR and MALDI-TOF MS (Electronic Supporting Information (ESI)).[10] The purities of **1-C$_n$**s were estimated from careful integration of the ^1H NMR spectrum, thermogravimetry, and differential thermal analysis (TG-DTA). We synthesized **1-C$_n$** with the alkyl chain lengths from pentyl (C5) to pentadecyl (C15) derivatives.

The thermal properties for the synthesized porphyrins were measured by TG-DTA and differential scanning calorimetry (DSC). From TG-DTA analyses (temperature range 30–600 °C, with a heating rate of $10\,°C\,min^{-1}$ under nitrogen), the decomposition temperature (2 wt % of initial weight loss) was more than 230 °C, and DTA peaks (corresponding to melting points) of the porphyrins were observed at less than 100 °C, so that the temperature range for DSC analyses was from −100 to 100 °C, with heating and cooling rates of $10\,°C\,min^{-1}$ under nitrogen. For example, the DSC chart of **1-C₁₂** is shown in Figure 2; the first and second heating scans of the molecule exhibited a sharp endothermic peak at ca. −6 °C, and a corresponding exothermic peak at ca. −21 °C, indicating that this molecule behaves like a liquid below RT. **1-C₅** and **1-C₆** melted at 78.6 and 83.9 °C, respectively, and did not show corresponding exothermic peaks, indicating that they were amorphous. For **1-C₇**, **1-C₈**, and **1-C₉**, no peaks were observed from −100 to 100 °C. The endothermic peaks of **1-C₁₀** and **1-C₁₁** were observed at −40 and −30 °C in the first and second heating scans, respectively. The corresponding exothermic peak of **1-C₁₀** was very weak and that of **1-C₁₁**, although very weak or broad, was observed at −23 °C. For **1-C₁₅**, the endothermic peak of the second scan was observed above 25 °C, indicating that it did not behave as a liquid at RT; therefore, the liquid range of the alkyl chain lengths are from C₁₀ to C₁₄ derivatives. It seems that **1-C$_n$**s have two phases, the liquid and solid phases, similar to the liquid fullerenes.[6] For example, **1-C₁₄** was obtained in the form of oil, but slowly solidified. **1-C₁₂** or the other molecules may behave
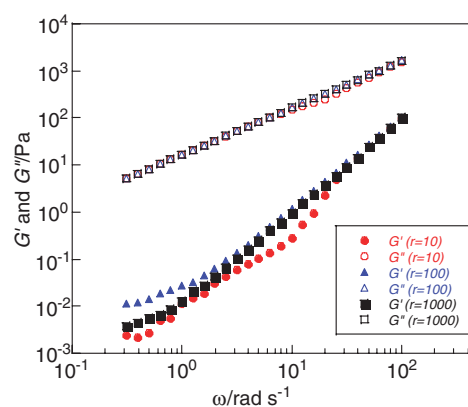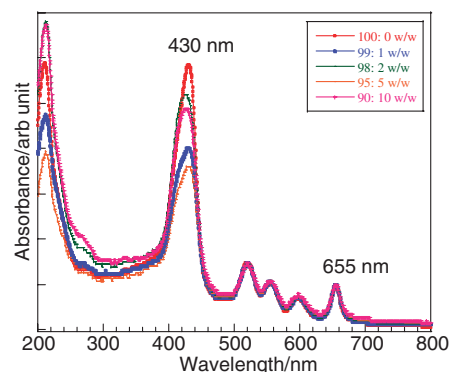
Figure 4. Normalized absorption spectra based on 655 nm for **1-C₁₂**/C₆₀ (w/w) on spin-coated film in air.

in the same manner. Before solidification, we observed the liquid-like behavior of the porphyrins and handled them as liquids. Upon heating, the solidified **1-C₁₄** melted and the liquid phase reappeared (ESI).

To obtain verification of liquid properties, we measured rheological properties for fluid **1-C₁₂** at 25 °C. Over the measured angular frequency (ω) range and the strain amplitude (γ) of 10, 100, and 1000, the loss modulus (G'') was higher than the storage modulus (G'), thus suggesting liquid-like behavior (Figure 3). When γ used was 0.01, 0.1, and 1, G' was not stable, also suggesting liquid-like behavior. The frequency dependence also indicated that there exist a number of components with a long relaxation time that might reflect cluster formation and complex dynamics. The complex viscosity (η^*) of **1-C₁₂** was ca. 16.5 Pa s as shown in Figure S-1 (ESI). The viscosity (η: Pa s) of **1-C₁₂** is also shown in Figure S-2.

We measured absorption and emission spectra to investigate the interaction of **1-C₁₂** with [60]fullerene (C₆₀) on spin-coated film. Absorption spectra for **1-C₁₂** with C₆₀ are shown in Figures S-3 (normalized based on 430 nm as Soret band) and S-4 (normalized based on 655 nm as Q band). In Figure S-3, the absorbance of Q band for **1-C₁₂** increased with addition of C₆₀. On the other hand, the absorbance of Soret band changed with addition of C₆₀, as shown in Figure 4. The emission spectra for
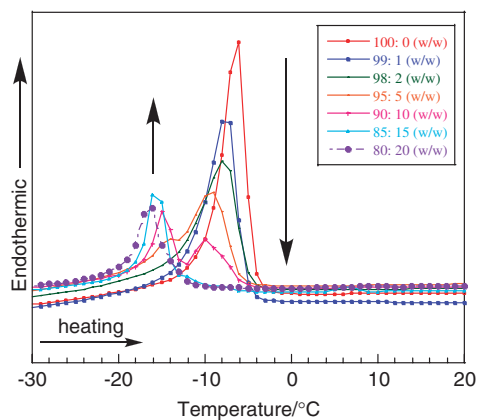
Figure 5. DSC chart of **1-C$_{12}$**/C$_{60}$ (w/w) at a heating and cooling rate of $10\,°C\,min^{-1}$ under nitrogen.

1-C$_{12}$ with C$_{60}$ using 430 nm as excitation wavelength are shown in Figures S-4 (normalized based on 660 nm) and S-5 (normalized based on 730 nm). The emission intensities of 730 and 660 nm changed, as shown in Figures S-4 and S-5, respectively. These results indicated that the intermolecular interaction between **1-C$_{12}$** and C$_{60}$ was a donor–acceptor and/or π–π interaction.[11]

It seems that **1-C$_n$** molecules would be useful as dispersion media of C$_{60}$ and/or CNTs. DSC chart of **1-C$_{12}$**/C$_{60}$ (w/w) (2nd heating scan) is shown in Figure 5. The melting points of **1-C$_{12}$** gradually decreased with addition of C$_{60}$, and a new endothermic peak was observed around $-14.5\,°C$ with addition of 5 wt % of C$_{60}$, although the melting point of **1-C$_{12}$** remained constant. Increasing the ratio of C$_{60}$ resulted in a peak and the melting point of **1-C$_{12}$** disappeared. The powder X-ray diffraction analysis (XRD) patterns of **1-C$_{12}$** also changed with addition of C$_{60}$. The details are described elsewhere.

In summary, the RT liquid porphyrins could be obtained by attaching long alkoxy chains to TPP. They would be new candidates for a dispersion medium for C$_{60}$ and/or CNTs by intermolecular π–π interaction, and possibly create new optical and electrical functionalities such as energy transfer and charge separation. They would also be used to create useful materials such as bucky-gels and liquid fullerenes. Electronic applications such as organic solar cells and electrochemical cells are now in progress.

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