



Short communication

Solubility of trifluoroethoxyphthalocyanines and -subphthalocyanines in liquid and supercritical carbon dioxide

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ABSTRACT

In an analysis of the solubility of a wide range of phthalocyanines (Pcs) and its analogues (SubPcs) in liquid and/or supercritical CO₂, compounds with trifluoroethoxy substituents were found to exhibit high solubility. To our knowledge, this is the first example of Pc compounds soluble in 100% CO₂. This unprecedented unique property of trifluoroethoxy substituted Pcs might have particular applications in catalysis in organic reactions as well as dyes for solar cells by CO₂ delivering coatings.

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1. Introduction

Global increase in environmental awareness has augmented the issue of green chemistry in the recent years [1]. Accordingly, the use of environmentally benign solvents, for instance, supercritical fluids [2] has been one of the leading research areas of green chemistry. Liquid CO₂ and/or supercritical CO₂ (scCO₂) are such solvents because they are naturally abundant, noninflammable, renewable, relatively nontoxic and readily evaporating. They have recently emerged as a way to solvate otherwise insoluble organic molecules and have been used as a reaction media for chemical reactions [3]. Liquid or scCO₂ also has unique and valuable potential in materials science as it is used as a solvent in polymer synthesis and processing [4] and as a medium for delivering coatings [5]. On the other hand, phthalocyanines (Pcs) have drawn substantial interest in a wide range of applications [6,7]. Pcs are employed as effective catalysts in a number of reactions as well [8]. However, the low solubility of Pcs in common organic solvents is notorious [7]. Recently, we came across the unique non-aggregation property of trifluoroethoxy (TFEO) coated phthalocyanines conjugated with deoxyribonucleosides, which are suitable for PDT agents [9a]. We also synthesized TFEO-coated binuclear Pc wherein the two Pcs are covalently linked with a

conjugated rigid di-yne spacer and noted its prominent avoidance of intermolecular aggregation [9b]. As part of our ongoing research programs directed to the development of novel functionalized Pcs and the synthesis of fluorine-containing biologically active compounds [9–11], we disclose herein the solubility of a wide range of Pc compounds in liquid CO₂ and scCO₂ to explore the effect of different types of peripheral substitution and structural modifications on the solubility properties of Pcs and Pc analogues such as subphthalocyanines (SubPcs). To our knowledge, no Pc compounds have previously been reported to be soluble in 100% CO₂.

2. Results and discussion

The MPcs and H₂Pcs shown in Fig. 1 were found to dissolve in liquid CO₂ and/or scCO₂. Over sixty Pc compounds and analogues did not: Co, Cu, Zn and Al tetra-sulfonated Pcs, H₂, Fe, Co and Cu tetra- and octa-carboxylated Pcs [11a], Zn and Co tetra- and octa-nitroPcs (at the α- and/or β-positions) [11b], H₂, Fe, Co, Cu, Zn and Ni tetra-*tert*-butyl Pcs [11c], H₂ and Zn tetraneopentoxypcs [11c], tetra- and octa-butyloxy Pcs [11d], crowned Pcs [11e], Fe tetra- and octadecyloxy-carbonylated Pcs [11f], Fe tetranitro and -amino Pcs (at the α- and/or β-positions) [11g], H₂ and ZnPcs with eight triethylene units [11h], H₂ and/or ZnPcs with tetra-alkyl-imides (decyl, benzo-15-crown-5-yl, adamantyl, anthraquinonyl alkyl groups) [11i], Co and Fe tetra- [11f] or octadecylimino Pcs [11j], Fe hexadecachloro and octacyano Pcs [11f], Co and Cu *tetrakis*(alkylammonio) Pc [11k], optically active binaphthyl-linked Pcs [11l], FePcs with electron-releasing groups [11m], dodeca-chlorinated

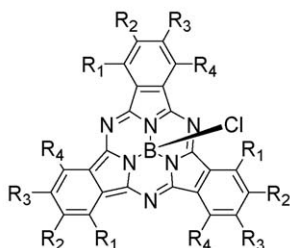
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- 1a:** 16(CF₃CH₂O)ZnPc: M = Zn, R₁~R₄ = CF₃CH₂O-
1b: 8α(CF₃CH₂O)ZnPc: M = Zn, R₁ = R₄ = CF₃CH₂O-, R₂ = R₃ = H
1c: 8β(CF₃CH₂O)ZnPc: M = Zn, R₁ = R₄ = H, R₂ = R₃ = CF₃CH₂O-
1d: 16(F)ZnPc: M = Zn, R₁~R₄ = F
1e: 4(*t*-Bu)ZnPc: M = Zn, R₂ or R₃ = *t*-Bu, R₁ = R₄ = R₃ or R₂ = H
1f: 16(CF₃CH₂O)H₂Pc: M = H₂, R₁~R₄ = CF₃CH₂O-
1g: 8α(CF₃CH₂O)H₂Pc: M = H₂, R₁ = R₄ = CF₃CH₂O-, R₂ = R₃ = H



- 2a:** 12(CF₃CH₂O)SubPc: R₁~R₄ = CF₃CH₂O-
2b: 3(*t*-Bu)SubPc: R₂ or R₃ = *t*-Bu, R₁ = R₄ = R₃ or R₂ = H

Fig. 1. Structures and abbreviations used for the compounds in this study that were found to dissolve in liquid CO₂ and/or scCO₂.

subPc [11n], tetra-*tert*-butylated Zn, optically active H₂ and Cu [11o] and tetra- and octa-*tert*-butylated Lu pyrazinoporphyrazines [11p], Mg, Cu, Co, Zn, and Ni tetra-*tert*-butylated tetraazaporphyrins [11q], naphthalocyanine sandwich compounds [11r], Si 2,3-pyridoporphyrazines with bulky axial ligands [11s], hydrogenated tetraazaporphyrins (chlorins, bacteriochlorins, and isobacteriochlorins) [11t], low symmetry Pc derivatives [11u] and Si complexes of *tert*-butylated triazacorrole [11v] and a Pc dendrimer [11w].

Only Pcs with trifluoroethoxy groups were found to exhibit a high level of solubility, Table 1 and Fig. 2. Several other trends were observed in the data. Firstly, solubility in liquid CO₂ is consistently higher than in scCO₂, since scCO₂ is a mixture of both gas and liquid. Secondly, metal complexes are more soluble than H₂Pcs (**1a** vs. **1f** and **1b** vs. **1g**). Thirdly, when the same number of a particular

Table 1

Apparent solubility of Pcs and SubPcs in liquid CO₂ and scCO₂.

Compound	In liquid CO ₂	In scCO ₂
1a: 16(CF ₃ CH ₂ O)ZnPc	++	+
1b: 8α(CF ₃ CH ₂ O)ZnPc	+	—
1c: 8β(CF ₃ CH ₂ O)ZnPc	±	—
1d: 16(F)ZnPc	—	—
1e: 4(<i>t</i> -C ₄ H ₉)ZnPc	—	—
1f: 16(CF ₃ CH ₂ O)H ₂ Pc	+	—
1g: 8α(CF ₃ CH ₂ O)H ₂ Pc	±	—
2a: 12(CF ₃ CH ₂ O)SubPc	+++	++
2b: 3(<i>t</i> -C ₄ H ₉)SubPc	++	±

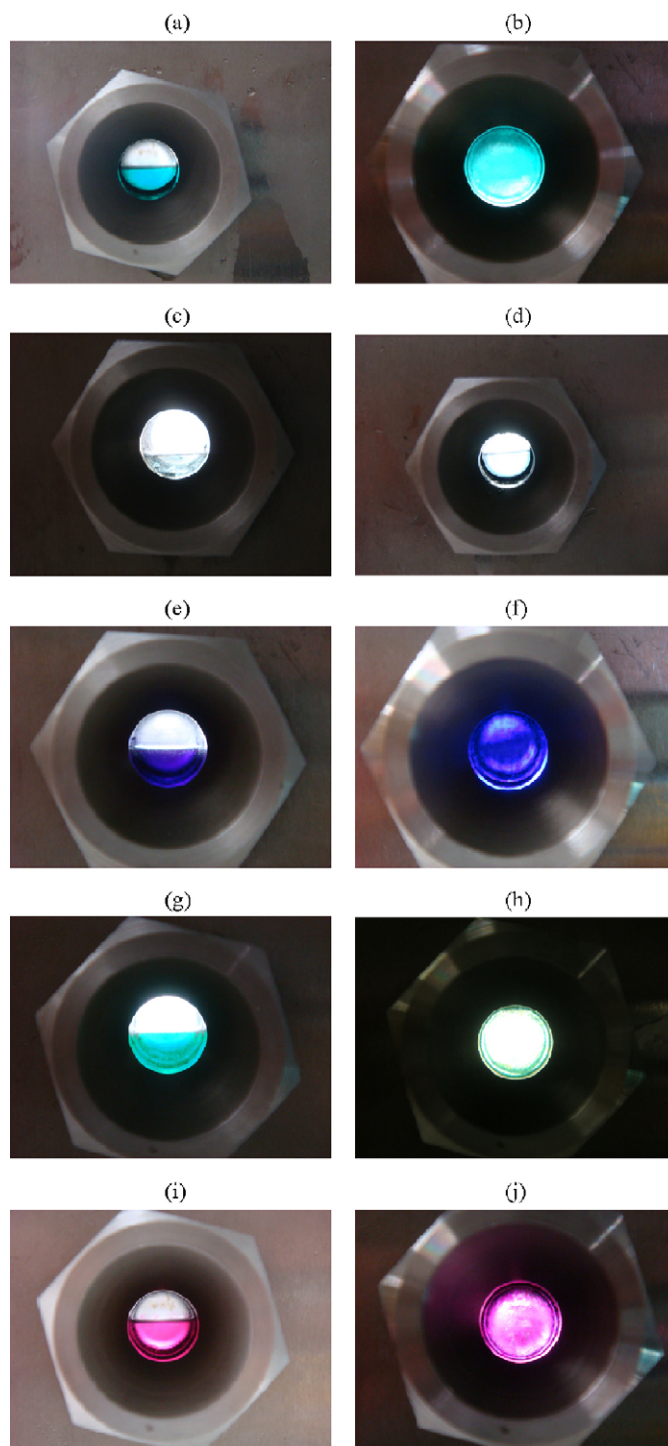


Fig. 2. Solubility of some of the compounds in liquid CO₂ and scCO₂. (a) **1a** in liquid CO₂ (4.4 MPa at 8 °C), (b) **1a** in scCO₂ (7.2 MPa at 49 °C), (c) **1b** in liquid CO₂ (4.6 MPa at 9 °C), (d) **1c** in liquid CO₂ (4.5 MPa at 5 °C), (e) **2a** in liquid CO₂ (4.8 MPa at 7 °C), (f) **2a** in scCO₂ (7.2 MPa at 48 °C), (g) **1f** in liquid CO₂ (4.3 MPa at 5 °C), (h) **1f** in scCO₂ (7.2 MPa at 47 °C), (i) **2b** in liquid CO₂ (4.3 MPa at 5 °C) and (j) **2b** in scCO₂ (7.1 MPa at 48 °C).

substituent are linked at the α- and β-positions, compounds with substituents at the α-positions have higher solubility (the properties of **1b** and **1c** were compared). The substituents at the α-positions generally stretch above and below the Pc plane (normal to the Pc plane) due to the presence of a substituent on a neighbouring isoindole moiety [12], while those at the β-positions stretch outwards radially when viewed from the center of the

ligand cavity. The final trend observed was an enhanced solubility of SubPcs relative to ZnPcs (**2a** vs. **1a**). This is probably related to the fact that SubPcs have cone-shaped structures [13], while MPcs are planar [12c]. *Tert*-butylated SubPc **2b** was the only non-fluorinated compound which dissolved in liquid CO₂, Table 1 and Fig. 2.

Compounds containing multiple fluorine typically exhibit low solubility in polar and hydrophobic solvents. Although CO₂ is non-polar due to the C_∞ molecular symmetry, there is still a marked electronegativity difference between the carbon and oxygen atoms. It has been reported previously that compounds with polar fluorine-containing alkyl chains exhibit enhanced solubility in liquid CO₂ and scCO₂ [3,14]. Although the reason for this has not been fully elucidated, it has been postulated based on an NMR study that an increase in the van der Waals interactions between the fluoroalkylated solute and the solvent is responsible for this phenomenon [15].

3. Conclusion

In conclusion, we came across that Pc compounds with trifluoroethoxy substituents exhibit high solubility in liquid and/or supercritical CO₂. To our knowledge, this is the first example of Pc compounds soluble in 100% CO₂. Since phthalocyanines are used in many practical applications [6,7], the solubility of trifluoroethoxy Pcs in liquid CO₂ and scCO₂ may prove to be of considerable interest in fields such as catalysis in organic reactions as well as dyes for solar cells by CO₂ delivering coatings. Further application of this phenomenon is now under investigation.

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