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"Conformational" Solvatochromism: Spatial Discrimination of Nonpolar Solvents by Using a Supramolecular Box of a π-Conjugated Zinc Bisporphyrin Rotamer**

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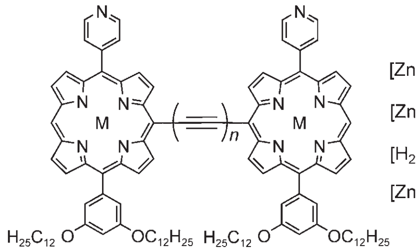
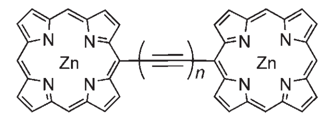
"Solvatochromism" is the ability of chromophoric molecules to change their absorption and/or luminescence colors as a result of a change in solvent polarity.[1–5] In principle, solvatochromic shifts are caused by a change in the energy gap between a ground state and excited state of different polarities, since a change in the solvent polarity leads to differential stabilization of these electronic states. Therefore, specific interactions between chromophore and solvent molecules result in variations in the wavelength, intensity, and shape of the absorption and/or luminescence spectra. Recent examples of particular interest include conjugated polymers that change their conformation and give rise to a solvatochromic response.[4] From this general understanding of solvatochromism, one may simply assume that the color of a chromophoric molecule hardly depends on the chemical structures of solvents when their polarities are, for example, equally very low.[5] Here we report the interesting phenomenon that a dialkynylene-bridged zinc bisporphyrin rotamer ($[\mathrm{ZnP}(\equiv)_2]$) shows an explicit solvatochromic response to nonpolar solvents with low dielectric constants (2.23–2.57). To our surprise, it can discriminate the regioisomers of xylene.

Zinc complexes $[\mathrm{ZnP}(\equiv)_n]$ ($n = 1$, 2, and 4) bearing two meso-pyridyl (Py) groups are designed to form a box-shaped cyclic tetramer in nonpolar solvents through Zn–Py coordination (Scheme 1). The assembling behavior of newly synthesized $[\mathrm{ZnP}(\equiv)_2]$ was unambiguously characterized by ^{1}H NMR, absorption, and emission spectroscopy, along with size-exclusion chromatography (SEC; see Figure S1 in the Supporting Information).[6] As reported in previous studies,[7–9] the $[\mathrm{ZnP}(\equiv)_1]$ monomer adopts exclusively a planar conformation in its cyclic tetramer ($[\{\parallel \mathrm{ZnP}(\equiv)_1\}_4]$), while longer alkynylene versions $[\{\mathrm{ZnP}(\equiv)_n\}_4]$ ($n = 2$, 4) exist as a mixture of the two conformationally isomeric tetramers $[\{\perp \mathrm{ZnP}(\equiv)_n\}_4]$ and $[\{\parallel \mathrm{ZnP}(\equiv)_n\}_4]$. The cyclic tetramers composed of $[\perp \mathrm{ZnP}(\equiv)_n]$ are chiral, and that with $n = 4$ ($[\{\perp \mathrm{ZnP}(\equiv)_4\}_4]$) has been demonstrated to sense the absolute structures of asymmetric hydrocarbon solvents.[9] In the course of these studies, we noticed that the colors of solutions of $[\mathrm{ZnP}(\equiv)_2]$ in benzene and CCl_4 are quite different from one another (Figure 1a), even though their dielectric constants are nearly identical. The absorption spectrum of a solution of $[\mathrm{ZnP}(\equiv)_2]$ in benzene showed Soret and Q bands at 447 (S_I) and 626 nm (Q_I), respectively (Figure 1a, green line). In contrast, the absorption profile in CCl_4 was considerably different, with the Soret and Q bands appearing at 447 (S_I)/483 (S_{II}) and 686 nm (Q_{II}), respectively (Figure 1a, red line). By reference to our previous studies on a derivative of $[\mathrm{ZnP}(\equiv)_2]$ with TMS-ethynyl groups at the meso positions and of $[\mathrm{ZnP}(\equiv)_4]$,[8] together with the (TD)DFT-simulated absorption bands of a dialkynylene-bridged zinc bisporphyrin reference $[\mathrm{ZnP}(\equiv)_2{}^*]$ with dihedral angles of 0 and 90° (B3LYP/6-31G*; see Figure S2 in the Supporting Information),[6] the green and orange-colored absorption spectra in Figure 1a can be assigned to the conformational isomers $[\{\perp \mathrm{ZnP}(\equiv)_2\}_4]$ and $[\{\parallel \mathrm{ZnP}(\equiv)_2\}_4]$, respectively. The box shape of $[\{\mathrm{ZnP}(\equiv)_2\}_4]$ seems essential for the observed solvatochromic response, since the absorption spectral profile of the free-base $H_2P(\equiv)_2$



$[\mathrm{ZnP}(\equiv)_1]$: M = Zn, $n = 1$
$[\mathrm{ZnP}(\equiv)_2]$: M = Zn, $n = 2$
$[\mathrm{H_2P}(\equiv)_2]$: M = H_2, $n = 2$
$[\mathrm{ZnP}(\equiv)_4]$: M = Zn, $n = 4$



$[\mathrm{ZnP}(\equiv)_2{}^*]$: $n = 2$
$[\mathrm{ZnP}(\equiv)_4{}^*]$: $n = 4$

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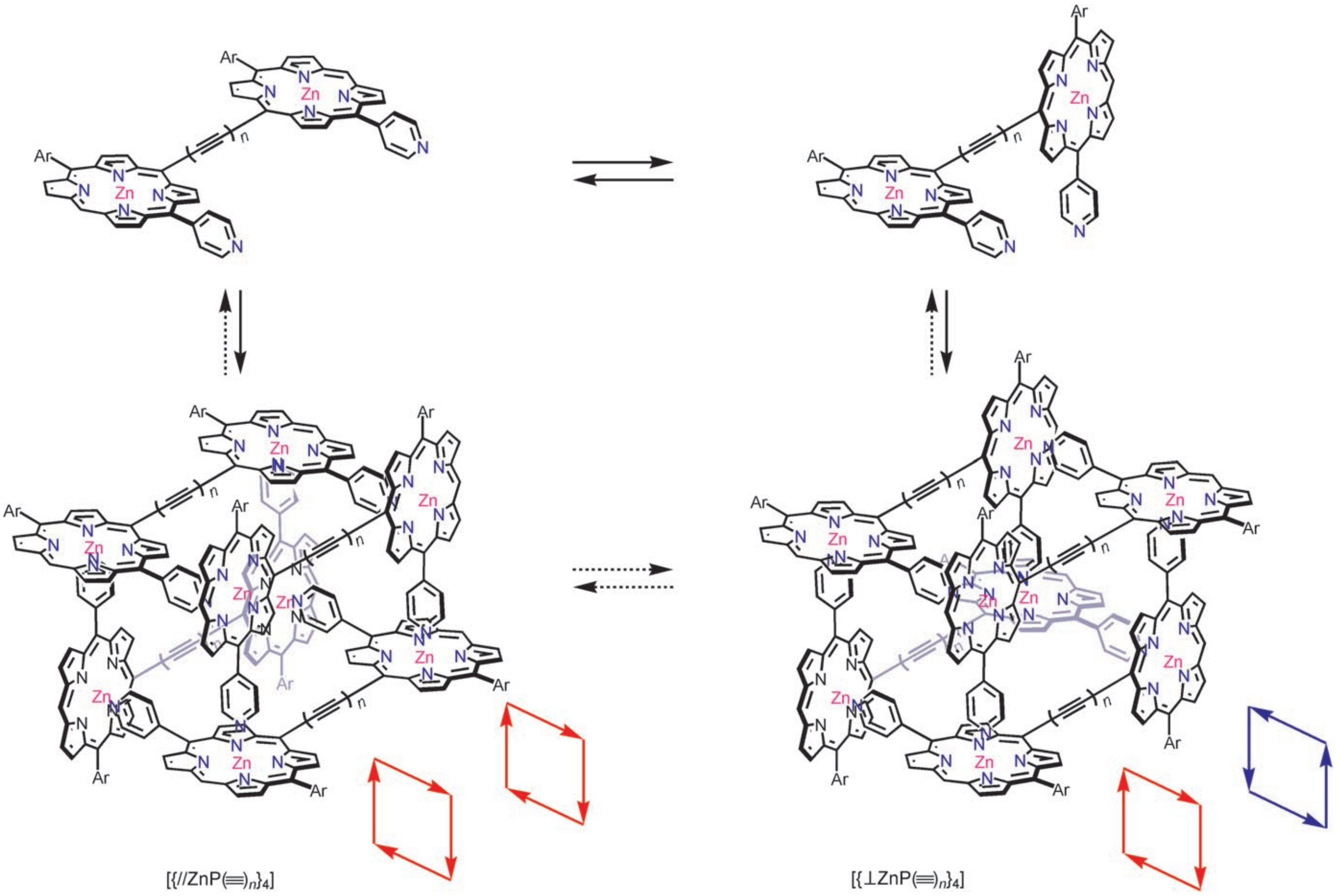

Scheme 1. Oligoalkynylene-bridged zinc bisporphyrin complexes $[\mathrm{ZnP}(\equiv)_n]$ ($n = 1$, 2, and 4) and their cyclic tetramers. Red and blue arrows indicate the directions of the dipole moments.

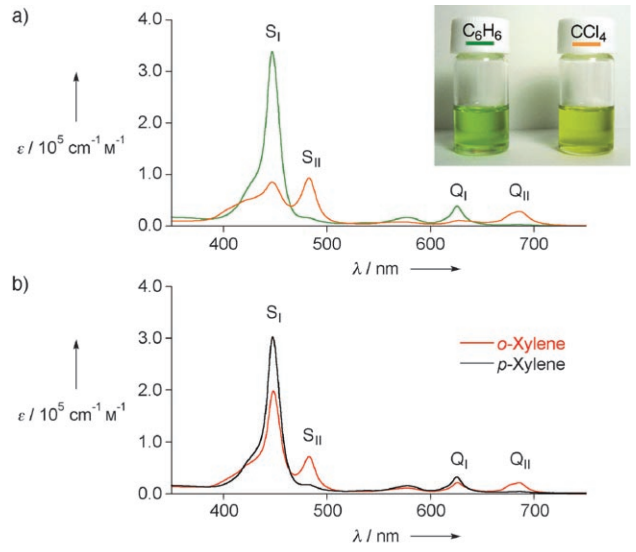

Figure 1. Absorption spectra of $[\{\mathrm{ZnP}(\equiv)_2\}_4]$ at 20 °C in a) benzene (green) and CCl_4 (orange), and b) *o*- and *p*-xylene (red and black, respectively). The inset shows photographs of solutions of $[\{\mathrm{ZnP}(\equiv)_2\}_4]$ in benzene (left) and CCl_4 (right).

did not vary when the solvent was changed from benzene to CCl_4 (see Figure S3 in the Supporting Information).[6]

In [D$_6$]benzene at 20 °C, assembled $[\mathrm{ZnP}(\equiv)_2]$ showed two sets of upfield-shifted signals at δ 2–3.5 and 5.5–6.5 ppm which could be assigned to the *ortho*- and *meta*-H atoms of the meso-pyridyl groups, respectively, upon coordination to the zinc porphyrin moieties (Figure 2a). This feature most likely originates from the assembly of $[\mathrm{ZnP}(\equiv)_2]$ into the box-shaped $[\{\perp \mathrm{ZnP}(\equiv)_2\}_4]$, where the inner and outer *ortho*- and *meta*-H atoms of the coordinating pyridyl groups can be discriminated from one another by NMR spectroscopy (Scheme 1).[8] When this solution was evaporated to dryness, and the residue was re-dissolved in CCl_4, an extremely slow transformation of $[\{\perp \mathrm{ZnP}(\equiv)_2\}_4]$ into $[\{\parallel \mathrm{ZnP}(\equiv)_2\}_4]$ took place. As shown in Figure 2b, the eight characteristic β pyrrole signals, initially observed at δ 6.8–11 ppm, disappeared gradually with time, and a new set of eight β-pyrrole signals appeared. This process was accompanied by a change in the absorption spectra, as shown in Figure 1a (from the green to the red curve), which finally subsided after 16 days. An excellent correlation was found between the relative intensity of the Q_I/Q_{II} absorption bands and the $[\{\perp \mathrm{ZnP}(\equiv)_2\}_4]/[\{\parallel \mathrm{ZnP}(\equiv)_2\}_4]$ ratio determined by ^{1}H NMR spectroscopy. This correlation allows convenient evaluation of the ratio of the tetrameric conformers by absorption spectroscopy (see below).

Cyclic tetramer $[\{\mathrm{ZnP}(\equiv)_2\}_4]$ can discriminate between benzene and CCl_4, and even the regioisomers of xylene

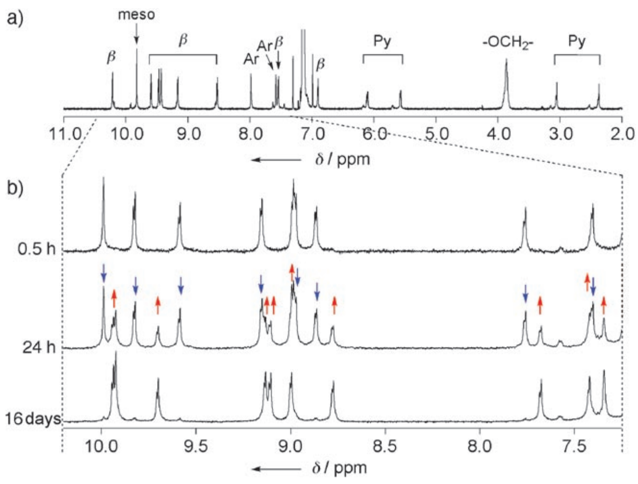

Figure 2. a) ^{1}H NMR spectrum ($\delta = 2.0$–11.0 ppm) of $[\{\mathrm{ZnP}(\equiv)_2\}_4]$ at 20 °C in [D$_6$]benzene, and b) its time-dependent change ($\delta = 7.2$–10.2 ppm) after a change in the solvent to $\mathrm{CCl_4}$.

(Figure 1 b). For convenience, "% stereoisomeric excess" (% *se*) values, defined by $([\{\parallel \mathrm{ZnP}(\equiv)_2\}_4]-[\{\perp \mathrm{ZnP}(\equiv)_2\}_4])/([\{\parallel \mathrm{ZnP}(\equiv)_2\}_4]+[\{\perp \mathrm{ZnP}(\equiv)_2\}_4]) \times 100$, were employed for illustrating the solvent-dependent conformational preferences of assembled $[\mathrm{ZnP}(\equiv)_2]$ (Figure 3). As described above, the % *se* values were estimated from the absorbances of the $\mathrm{Q_I}$ and $\mathrm{Q_{II}}$ bands. $[\mathrm{ZnP}(\equiv)_2]$ unit in the cyclic tetramer preferred to adopt a perpendicular conformation in *p*-xylene (entry 2; $se = -78\,\%$) but a planar conformation in *o*-xylene (entry 7; $se = 39\,\%$), while in *m*-xylene the mole ratio of $[\perp \mathrm{ZnP}(\equiv)_2]$ to $[\parallel \mathrm{ZnP}(\equiv)_2]$ was nearly unity (entry 6; $se = 2\,\%$). Since the dielectric constants of the regioisomers of xylene are again nearly identical (2.27 and 2.57), the solvatochromic response thus observed suggests that $[\mathrm{ZnP}(\equiv)_2]$ recognizes the shapes of solvent molecules when it forms the cyclic tetramer.[10–13] Equally interesting, non-aromatic hydrocarbons such as terpenes (entries 4 and 5; $se = -25$ and $-21\,\%$, respectively) were differentiated from terpinolene (entry 9; $se = 61\,\%$).

In contrast to $[\{\mathrm{ZnP}(\equiv)_2\}_4]$, $[\{\mathrm{ZnP}(\equiv)_1\}_4]$ and $[\{\mathrm{ZnP}(\equiv)_4\}_4]$, which possess one and four triple bonds in the spacer, respectively, were not solvatochromic in the nonpolar solvents examined (see Figure S4 in the Supporting Information),[6] which indicates that the spacer between the zinc porphyrin units in $[\mathrm{ZnP}(\equiv)_n]$ plays a critical role in the observed solvatochromic response. One of the most important factors in this respect is the π conjugation between the zinc porphyrin units. As fully substantiated experimentally,[14,15] bisporphyrins with a monoalkynylene bridge always adopt a planar conformation, and this is also the case for $[\mathrm{ZnP}(\equiv)_1]$ in its cyclic tetramer.[8a] Hence, $[\{\mathrm{ZnP}(\equiv)_1\}_4]$ cannot show conformational solvatochromism. On the other hand, the energy difference between the two conformers of reference $[\mathrm{ZnP}(\equiv)_4{}^*]$ was estimated by means of DFT calculations (B3LYP/6-31G*) to be negligibly small (0.09 kcal mol^{-1}; see Figure S5 in the Supporting Information).[6] This small energy difference may be one of the main reasons why $[\{\mathrm{ZnP}(\equiv)_4\}_4]$ does not show any solvatochromic responses. In contrast, since the calculated energy gap of 0.57 kcal mol^{-1} between $[\parallel \mathrm{ZnP}(\equiv)_2{}^*]$ and $[\perp \mathrm{ZnP}(\equiv)_2{}^*]$ (see Figure S5 in the Supporting Information)[6,16] is not negligible, it can be expected that $[\{\parallel \mathrm{ZnP}(\equiv)_2\}_4]$ will be preferred over $[\{\perp \mathrm{ZnP}(\equiv)_2\}_4]$. However, in some solvents, $[\{\perp \mathrm{ZnP}(\equiv)_2\}_4]$ rather than $[\{\parallel \mathrm{ZnP}(\equiv)_2\}_4]$ forms predominantly, which indicates the presence of some competing factors (Figure 3). A very likely candidate is a dipole–dipole interaction in the box-shaped assembly, which cannot be ignored in nonpolar solvents. As illustrated in Scheme 1, the dipole moments in $[\{\perp \mathrm{ZnP}(\equiv)_2\}_4]$ are more efficiently cancelled out than those in $[\{\parallel \mathrm{ZnP}(\equiv)_2\}_4]$, thereby giving a certain advantage to $[\{\perp \mathrm{ZnP}(\equiv)_2\}_4]$. We presume that the balance between these competing factors, that is, the preferences arising from π conjugation and dipole–dipole interaction, may vary depending on the solvents, whilst their dipole moments are equally low. More specifically, this change in balance may be caused by particular electronic and/or steric effects of caged solvent molecules within the cavity of the host $[\{\mathrm{ZnP}(\equiv)_2\}_4]$ (see Figure S6 in the Supporting Information).[6,12] Again, for $[\{\mathrm{ZnP}(\equiv)_4\}_4]$, whose covalently linked zinc porphyrin units are further apart from one another than those in $[\{\mathrm{ZnP}(\equiv)_2\}_4]$, the issue of dipole–dipole interactions is considered much less important. The large dimensions of the cavity and the negligible π conjugation between the zinc porphyrin units means that $[\{\mathrm{ZnP}(\equiv)_4\}_4]$ is intrinsically not capable of conformational solvatochromism.

In conclusion, we have found a new principle of solvatochromism for nonpolar solvents with low dielectric constants (2.23–2.57). This principle takes advantage of a confined

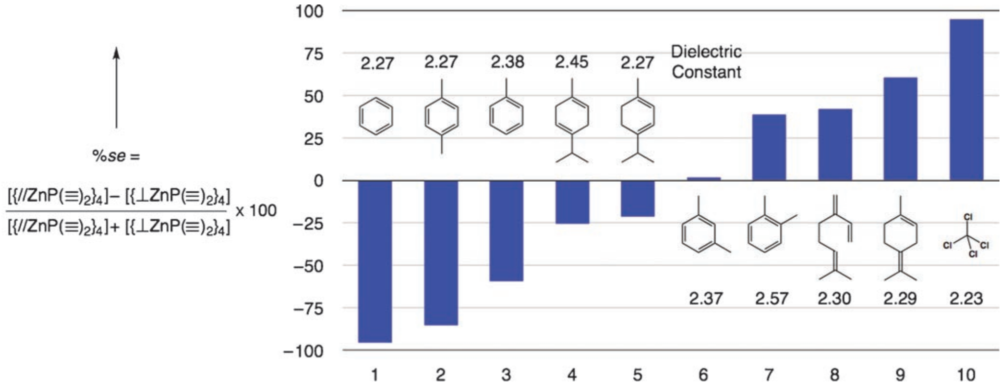

Figure 3. % Stereoisomeric excess (% *se*) values of $[\{\mathrm{ZnP}(\equiv)_2\}_4]$ in nonpolar solvents at 20 °C ($[\{\mathrm{ZnP}(\equiv)_2\}] = 5.9 \times 10^{-6}$ M).

chromophoric cavity, formed by the assembly of a π-conjugated rotamer with various degrees of π conjugation. In the assembly, the conformation of the rotamer is fixed as either planar (conjugated) or perpendicular (nonconjugated), which give rise to different absorption spectra. A solvatochromic response results because the ratio of the conformers of the tetrameric assembly changes depending on the solvent. This unique feature enables spectroscopic discrimination between benzene (dielectric constant 2.27) and CCl_4 (2.23) and, to our surprise, even the regioisomers of xylene (2.27 and 2.57). The principle of these phenomena can be referred to as "conformational" solvatochromism.

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