



## Chirality induction in binuclear phthalocyanine tweezers



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### ABSTRACT

A novel binuclear phthalocyanine tweezers, in which two zinc-phthalocyanine rings are linked to an optically active binaphthyl group through triazolyl linkages, was self-cyclized through triazolyl-to-zinc coordination bonds. An axially chiral *S*-binaphthyl group induced planar chirality in a slipped-cofacial stack of phthalocyanine moieties, and therefore displayed fluorescence with a good quantum yield ( $\Phi_F = 0.23$ ) and circularly polarized luminescence with a moderate intensity of dissymmetry factor ( $g_{lum} = -4 \times 10^{-4}$ ) in the near-infrared wavelength region.

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Asymmetric  $\pi$ -systems exhibit chiral electronic properties such as circular dichroism (CD)<sup>1,2</sup> and circularly polarized luminescence (CPL).<sup>3</sup> CPL-active chromophores are now emerging as privileged materials aimed at sophisticated optical devices<sup>4</sup> and enhanced chiroptical sensors.<sup>5</sup> The wavelength region of CPL is limited mainly to the visible region shorter than 650 nm with a few exceptions of lanthanide complexes,<sup>6</sup> although near-infrared (NIR) emission also points to similar applications.<sup>7</sup> Thus, NIR-CPL-active chromophores should provide a vital element for creating highly sophisticated organic optical materials. The present study demonstrates a novel molecular design of an organic NIR-CPL-active chromophore.

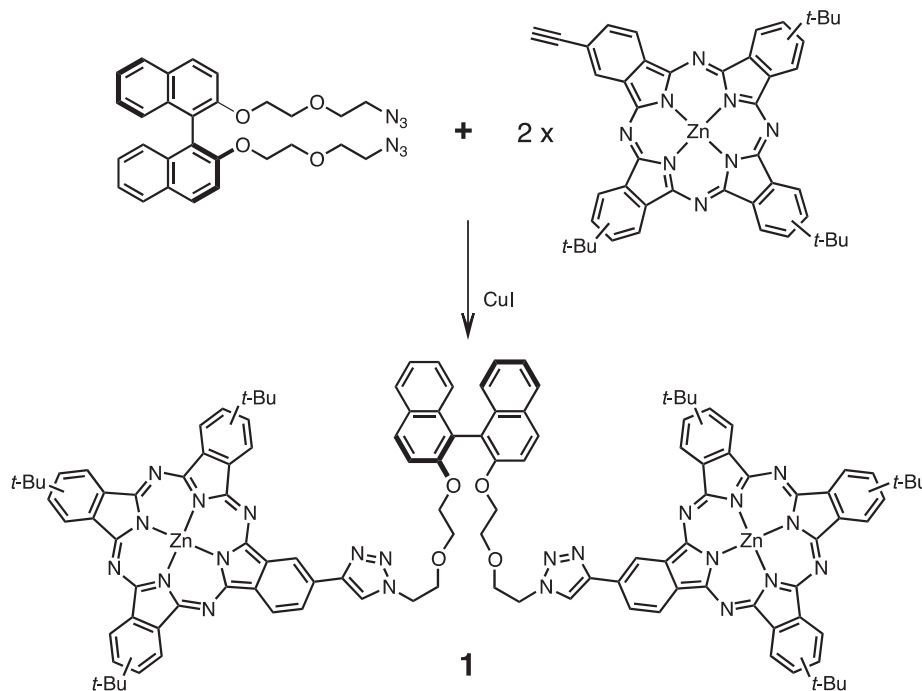
Metallophthalocyanines are superb NIR dyes and pigments for practical use because of their chemical and thermal robustness.<sup>8</sup> The expanded  $\pi$ -orbitals of phthalocyanines (Pcs) exhibit an exceptionally large extinction coefficient of the Q band. By contrast, persistent  $\pi$ -stacked interactions restrict potential applications especially in optical and photosensitizing materials, because the excited singlet is strongly deactivated in such aggregates. The organization of J-aggregates should be rational to overcome this problem. However, even if J-type aggregates are formed, the structural disorder often dissipates the photoexcited singlet.<sup>9</sup> By contrast, the discrete Pc dimers with a slipped-cofacial conformation resulting from intramolecular self-complementary coordination have been demonstrated to exhibit intense fluorescence.<sup>10–14</sup> Therefore, a molecular design that imparts chirality to the fluorescent Pc dimers is quite attractive for developing NIR-CPL materials.

A 1,2,3-triazolyl ligand can coordinate to the central metal of porphyrinoid in a self-complementary manner and form a slipped-cofacial dimer,<sup>15</sup> although this has not been applied to Pcs yet. The triazolyl ring is derived readily by a copper(I)-catalyzed 1,3-dipolar Huisgen cycloaddition of azide with alkyne, the so-called 'click' reaction,<sup>16</sup> which is appropriate for covalently linking two or more modular units. Here, we design binuclear Zn(Pc) tweezers **1** as a novel NIR-CPL material (Scheme 1). The axially chiral binaphthyl bridging group is expected to induce planar chirality effectively in the relative orientation of the orthogonally tethered Pc terminal through intramolecular self-complementary triazolyl-to-zinc coordination. The Huisgen cycloaddition of two ethynyl Zn(Pc) precursors<sup>17</sup> with an azide-terminated binaphthyl derivative gave **1** in excellent yield (97%).

The absorption spectra of **1** showed a split Q band at 677 and 694 nm (Fig. 1a), which is reminiscent of that of slipped-cofacial stacks of Pc,<sup>10–12</sup> as predicted by Kasha's molecular exciton theory.<sup>18</sup> The split Q band indicates the formation of a slipped-cofacial stack of Pc moiety of **1**, considering that the peripheral substitution of a triazolyl group does not cause substantial changes in the degenerated Q band without coordination interactions.<sup>19</sup> It is possible to form self-complementary coordination bonds in both intramolecular and intermolecular fashions. We found that **1** did not obey Beer's law at concentrations higher than  $7.0 \times 10^{-7}$  M. Upon titration with pyridine as a competitive ligand around  $7.0 \times 10^{-6}$  M, a spectral change through isosbestic points was observed (Fig. 1a), indicating that pyridine cleaved the intermolecular coordination bonds in the supramolecular polymer. By contrast, at concentrations less than  $7.0 \times 10^{-7}$  M, addition of excess

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Scheme 1. 'Click' synthesis of binuclear Zn(Pc) tweezers **1**.

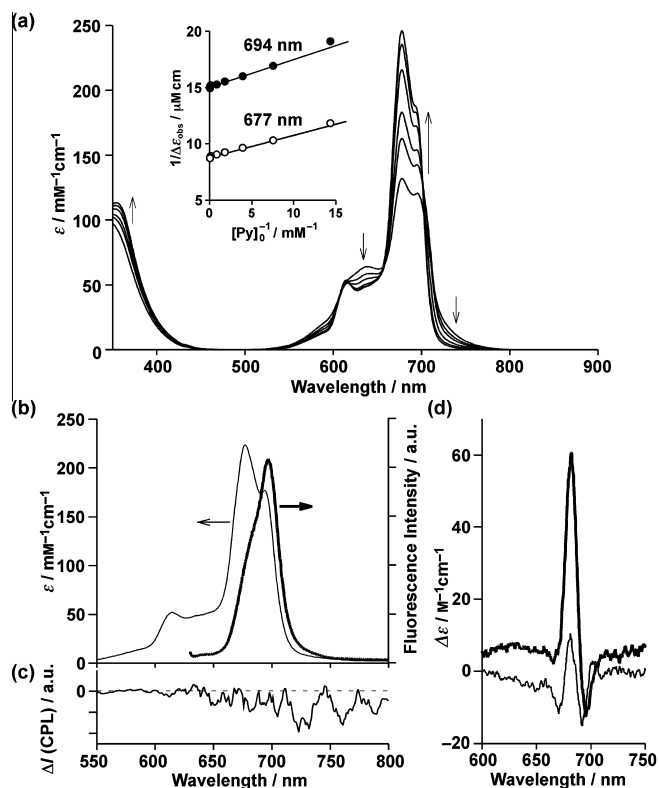


Figure 1. (a) Pyridine titration of **1** at ca.  $7.0 \times 10^{-6}$  M at 20 °C in toluene (pyridine: 0–1000 equiv). Inset shows the Benesi–Hildebrand plot at 694 (closed circle) and 677 nm (open circle). (b) Absorption (thin line) and fluorescence (thick line) spectra of **1** at  $3.0 \times 10^{-7}$  M in toluene. Fluorescence spectrum was recorded upon excitation at 620 nm. (c) CPL spectrum of **1** in toluene. (d) CD spectra of **1** at  $3.0 \times 10^{-7}$  M (thick line) and  $7.0 \times 10^{-6}$  M (thin line) in toluene.

pyridine caused no substantial spectral change,<sup>20</sup> suggesting that the intramolecular self-complementary triazolyl-to-zinc coordination is persistent enough to exclude competitive coordination of

the external ligand. In principle, the self-cyclization is preferable to supramolecular polymerization in terms of entropy.<sup>21</sup> However, supramolecular polymerization proceeded readily even under the diluted conditions. These observations suggest that the strain of the self-cyclized conformation destabilizes intramolecular coordination; this idea was supported by the following thermodynamic analysis.

The upper limit of the concentration for self-cyclization is indexed by the effective molarity ( $EM$ ) as the parameter;  $EM = K_{\text{close}}/K_{\text{open}}$ ,<sup>21</sup> which can be analyzed using a titration experiment. The spectral change displays a proportional relationship to the Benesi–Hildebrand approximation (inset in Fig. 1a) as follows.<sup>22</sup>

$$\Delta\epsilon_{\text{obs}}^{-1} = \{\Delta\epsilon \cdot K_{\text{obs}}\}^{-1}[\text{Py}]_0^{-1} + \Delta\epsilon^{-1}, \text{ wherein } [\text{Py}]_0 \gg [1]_0$$

Upon addition of pyridine, the supramolecular polymers were dissociated into  $1_n \cdot \text{Py}$  and then spontaneously self-cyclized as shown in Scheme 2, in which the spectral change reflects only the first binding step. The binding constant for the observed equilibrium is given as  $K_{\text{obs}} \approx [1_n \cdot \text{Py}]/[1_n][\text{Py}]$ . Consequently, the  $EM$  value was estimated roughly as  $5.6 \times 10^4 \text{ M}^{-1}$ , corresponding to a small free energy penalty,  $\Delta\Delta G = -RT \ln EM = -26 \text{ kJ mol}^{-1}$ , wherein  $R$  is the gas constant and  $T$  is the absolute temperature. The value denotes relatively unfavorable self-cyclization while supramolecular polymerization is preferable even in diluted conditions. Eventually, thermodynamic analysis elucidated that **1** adopted the self-cyclized conformation because of the sufficient binding strength of the triazolyl-to-zinc coordination bond despite the ring strain under sufficiently diluted conditions (less than the order of  $10^{-7}$  M).

In a noncoordinating solvent such as  $\text{CDCl}_3$  or toluene- $d_8$ , the  $^1\text{H}$  NMR spectra of **1** showed consistently broad signals, suggesting the formation of supramolecular polymer  $1_n$ . By contrast, in pyridine- $d_5$ , the persistent intramolecular coordination of **1** allowed the structural investigation of the self-cyclized conformation wherein pyridine- $d_5$  as the competitive ligand prevented the supramolecular polymerization but did not substantially disturb

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