Synthesis of covalently linked binuclear clamshell phthalocyanine by double-click reaction†

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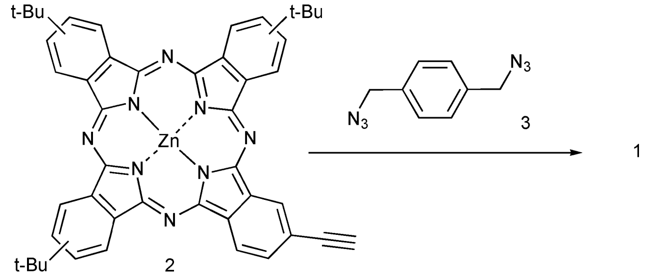
A novel covalently linked binuclear phthalocyanine 1 was synthesized by the "double-click" reaction. The UV-vis and fluorescence spectra and electrochemistry revealed that the geometry of 1 is a closed clamshell conformation in which a strong electronic interaction is observed between the two Pc moieties.

Phthalocyanines (Pcs), one of the best known π-conjugated disk-like molecules have attracted special interest for use in organic electronic devices.[1] Self-assembly and self-organization of Pcs into well-defined structures with nanometre dimensions are a highly active area of research in chemistry and material science.[2] Although many studies have been dedicated in this field, programmed assemblies of Pc units still have challenges. Recently azide/acetylene "click chemistry" has emerged as one of the most promising tools to build up polymers with unique architectures and networks under mild conditions;[3] however, there are few examples where the click reaction has been employed to prepare structural alignment of Pcs polymers.[4] We therefore came up with the idea to control the alignment of Pcs on polymers based on the click reaction (Fig. 1a). In this strategy, the minimum unit is binuclear phthalocyanine which should appear capable of closing in a flexible "clamshell"-like fashion by the strong π-interaction.[5] As our first step towards achieving this goal, we herein disclose the synthesis of novel covalently linked flexible binuclear phthalocyanine **1** by the use of "double-click" chemistry. Spectroscopic and electrochemical studies revealed that our binuclear Pc **1** shows expected remarkably flexible closed clamshell behavior (Fig. 1b).

1,4-Bis(1-(tri-*tert*-butylphthalocyaninate zinc(II))-1*H*-1,2,3-triazol-4-yl)benzene (**1**) was synthesized from 23-ethynyl-2(3),9(10),16(17)-tri-*tert*-butylphthalocyaninate zinc(II) (**2**)[6] and 1,4-bis(azidomethyl)benzene *via* "double-click" reactions by use of CuI and DMSO in 80% yield (Scheme 1).[7] The purity and identity of **1** were determined by reverse-phase HPLC, ^{1}H, NMR, and the isotopic patterns of Zn in MALDI-TOF MS spectra (see ESI).



Scheme 1 *Reagents and conditions*: 1,4-(N_3CH_2)C_6H_4 (0.5 equiv.), CuI (8 mol%), DMSO, 60 °C, 3 h, 80%.

The electronic absorption spectra in $CHCl_3$ in the concentration range 0.5 or 1.0×10^{-4} to 10^{-6} M are shown in Fig. 2. Whereas the reference mononuclear Pc **2** displays absorption spectra that are typical of monomeric species (Fig. 2b), the binuclear Pc **1** affords a substantial broadening of the Q-band centering on 681 nm and the usual B-band at 349 nm (Fig. 2a), which are indicative of aggregation phenomena. The observation of both a blue shifted Q-band peak at 633 nm and a red shifted 700–800 nm shoulder is attributed to mixed dimer types of H- and J-aggregation.[8] The shapes of the absorption spectra of **1** were independent of the concentration, which clearly indicates that an intramolecular assembly is responsible for this behavior, and the possibility of the imidazole moiety coordination to the zinc can be excluded.[9] These facts are consistent with the reported observation of binuclear Pcs ascertained as the closed clamshell conformation.[5] The clamshell conformation of **1** can be flexibly opened to non-aggregation by the addition of pyridine due to the coordination to the central Zn atom.[10] The broadened peak disappeared concurrently with the rise of an intense monomeric peak at 680 nm (dashed line in Fig. 2a). The height of the Q band at 680 nm is now almost double compered to the original one at 681 nm. These results support that the binuclear Pc **1** exists mainly as closed clamshell conformation with a minor open conformer. Similar pictures of UV-vis spectra of clamshell Pcs were reported.[5b,d,g,i] No significant alteration was observed in the case of Pc **2** (dashed line in Fig. 2b). A similar electronic absorption spectra of **1** and **2** were observed in toluene (Fig. S1 and S2 in ESI).

Steady-state fluorescence spectra in $CHCl_3$ were next investigated to probe the aggregation in **1** and **2** (Fig. 3). While Pc **2** showed strong fluorescence at 686 nm (fluorescence quantum yield $\Phi_f = 0.40$), the emission of binuclear Pc **1** was markedly quenched (λ_{em} = 687 and 710 nm; $\Phi_f = 0.010$). The phenomenon in **1** was identical to the reported result that the clamshell arrangement is non-fluorescent.[5] Although the phenomenon of quenching in clamshell Pcs is well known, the mechanism is not really clear. It should be based on the intramolecular self-quenching between the coupled halves of the binuclear species through several possible mechanisms including relaxation to triplet states and nonradiative vibrational relaxation.[5d] The red-shifted small peak at 710 nm was attributed to intramolecular J-aggregation, and disappeared by the addition of pyridine because of the disturbance of the assembly. Besides, addition of pyridine restored the fluorescence

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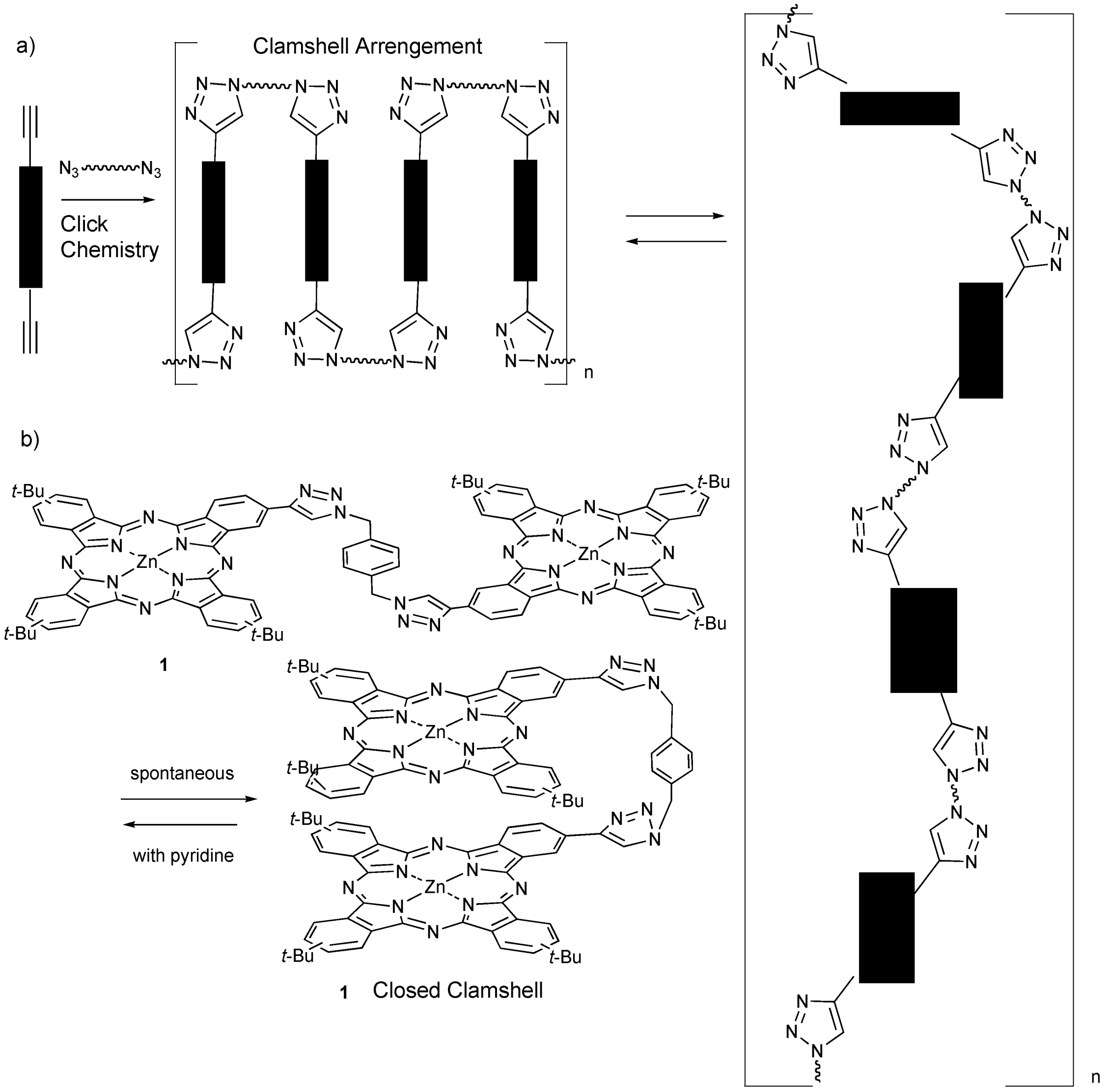

Fig. 1 a) Alignment control of Pcs based on the click chemistry. b) A novel covalently linked flexible binuclear phthalocyanine **1** with a clamshell conformation.

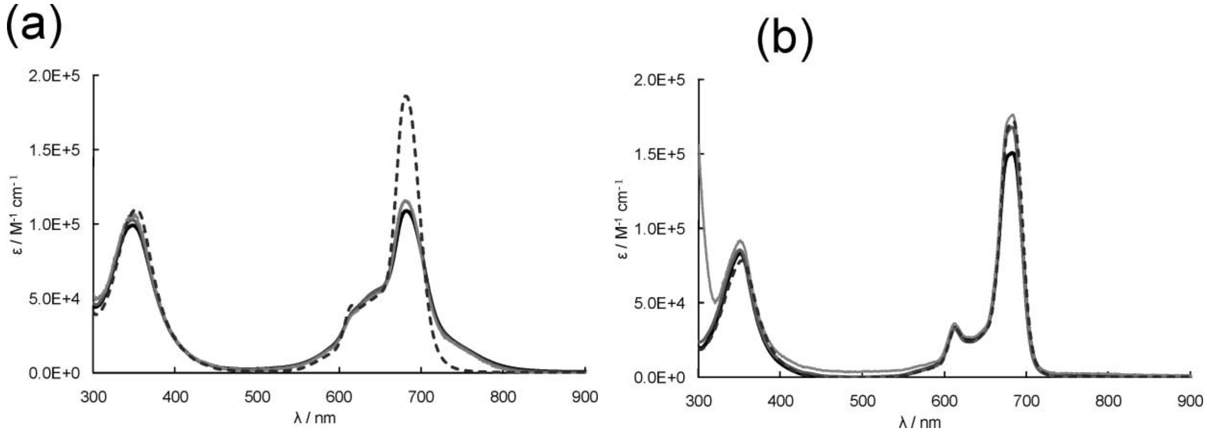

Fig. 2 UV-Vis spectra of **1** (a) and **2** (b) in $CHCl_3$. Solid line: 0.5×10^{-4}–10^{-6} M for **1**, 1.0×10^{-4}–10^{-6} for **2**; Dashed line: with 1 vol% of pyridine.

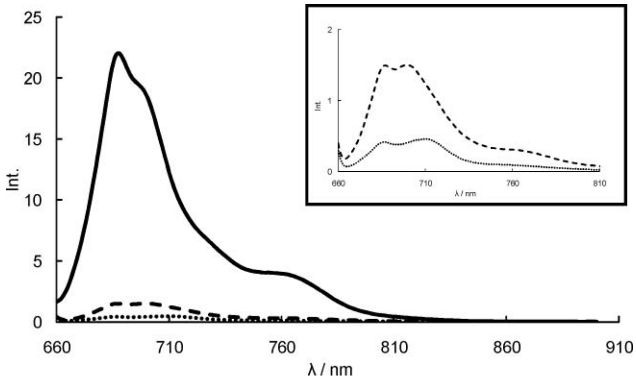

Fig. 3 Steady-state fluorescence spectra in $CHCl_3$. Solid line: **2**; Dotted line: **1**; Dashed line: **1** with 1 vol% of pyridine. Inset: enlarged view of spectra of **1**, before and after addition of pyridine.

with triple the Φ_f value ($\lambda_{em} = 687$ and 699 nm; 0.033). A similar phenomenon in steady-state fluorescence spectra of **1** and **2** was observed in toluene (Fig. S3 and S4 in ESI). In the measurement of time-resolved fluorescence decay in THF, lifetime τ_f of **1** 3.34 ± 0.04 ns was obtained with satisfactory mononexponential fit, approximately equal to 3.92 ± 0.04 ns of **2** (Fig. 4).[11,12] The τ_f did not seem to be significantly reduced though Pc-stacking gave strong quenching and corresponding low quantum yield in the emission spectra.[12]

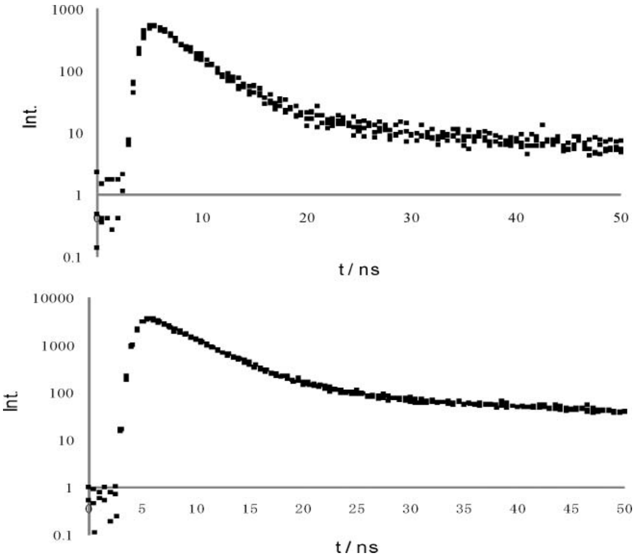

Fig. 4 Fluorescence decay of **1** (top) and **2** (bottom) in deaerated THF.

Table 1 Half-wave redox potentials of **1** and **2** (V *vs* Ag/AgNO$_3$) in THF containing 0.1 M of TBAPF

	$E_{1/2}^{ox2}$	$E_{1/2}^{ox1}$	$E_{1/2}^{red1}$	$E_{1/2}^{red2}$	$E_{1/2}^{red3}$	$E_{1/2}^{red4}$
1	0.447	0.205	−1.195	−1.360	−1.472	−1.903
2	0.500	0.312	−1.190	−1.424	−1.871	

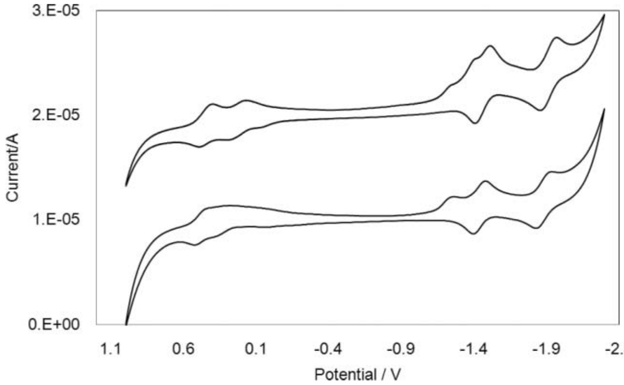

Fig. 5 Cyclic voltammograms of **1** (top) and **2** (bottom).

Table 2 Peak potentials of **1** and **2** (V *vs* Ag/AgNO$_3$) in THF containing 0.1 M of TBAPF

	$E_{1/2}^{ox2}$	$E_{1/2}^{ox1}$	$E_{1/2}^{red1}$	$E_{1/2}^{red2}$	$E_{1/2}^{red3}$	$E_{1/2}^{red4}$
1	0.475	0.235	−1.20[a]	−1.355	−1.455	−1.895
2	0.545	0.300	−1.18[a]	−1.410	−1.850	

[a] Only broad peaks were obtained.

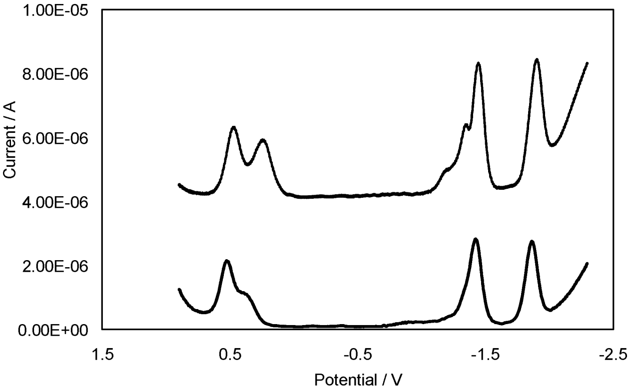

Fig. 6 Differential pulse voltammograms of **1** (top) and **2** (bottom).

Cyclic (CV) and differential-pulse voltammograms (DPV) in THF are summarized in Table 1/Fig. 5 and Table 2/Fig. 6, respectively. In the cathodic scan, both **1** and **2** showed the first irreversible reduction processes at *ca.* −1.19 V in a similar way. These may come from aggregation of Pc in the higher concentration, since only low resolved peaks were obtained in the DPV.[13] The second wave of **1** was split into two quasi-reversible one-electron processes at −1.360 V and −1.472 V per one Pc moiety in **1**, compared with one quasi-reversible two-electron −1.424 V of **2**. In the anodic scan of **1**, irreversible one-electron and quasi-reversible one-electron oxidation processes were obtained at 0.205 and 0.447 V, respectively. The binuclear Pc **1** is easier to be oxidized than mononuclear Pc **2** (0.312 and 0.500 V). These findings indicate that an intramolecular interaction exists between two Pc moieties in **1**. As seen in previous Pc oligomers, the potential between the first reduction and the first oxidation became smaller by the interaction of Pc moieties.[14]

In conclusion, we have synthesized binuclear phthalocyanine **1** by the use of "double-click" chemistry. The UV-vis and fluorescence spectra and electrochemistry revealed that the geometry of Pc **1** is the closed clamshell conformation whereby a strong electrochemical interaction is observed between the two Pc moieties. The clamshell can be easily opened by the addition of pyridine. These facts are great advantages for the construction of polymers with programmed assemblies of Pcs under click chemistry.[4] Polymer synthesis is now under investigation based on this strategy.

Acknowledgements

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