

Self-assembly of a π -electronic amphiphile consisting of a zinc porphyrin–fullerene dyad: formation of micro-vesicles with a high stability†

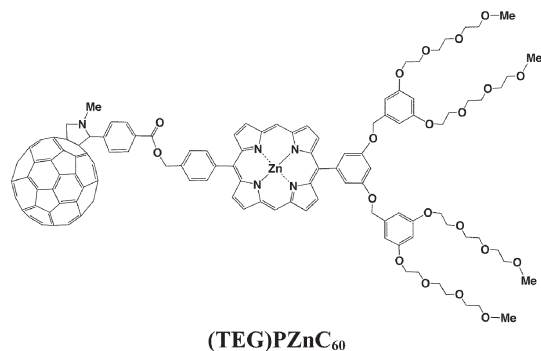
Richard Charvet, Dong-Lin Jiang and Takuzo Aida*

ERATO Nanospace Project, Japan Science and Technology Agency, clo National Museum of Emerging Science and Innovation, 2-41 Aomi, Koto-ku, Tokyo, 135-0064, Japan. E-mail: aida@macro.t.u-tokyo.ac.jp; Fax: +81-3-3570-9183; Tel: +81-3-3570-9182

Received (in Cambridge, UK) 17th June 2004, Accepted 31st August 2004
First published as an Advance Article on the web 11th October 2004

An amphiphilic zinc porphyrin–fullerene dyad appended with triethyleneglycol chains in aqueous media forms uniformly-sized multilamellar vesicles with a mean diameter of 100 nm that are thermally stable and robust against membrane lysis with surfactants.

Implementation of certain functions to vesicular assemblies is an important subject for the development of new applications related to the guest-entrapping capability of such nano-objects. To fabricate these vesicles, functional units have been incorporated into lipid molecules, where specific packing of hydrophobic alkyl chains plays an important role for the stability of the vesicular membrane.¹ Here we report that a non-lipid type π -electronic amphiphile consisting of a zinc porphyrin–fullerene dyad ((TEG)PZnC₆₀) forms uniformly sized micro-vesicles in aqueous media.² As porphyrin derivatives and fullerenes can electronically interact with one another under certain conditions,³ these molecules when appropriately combined are expected to serve as alkyl chain substitutes for self-assembly. While ordinary lipid vesicles are easily disrupted upon addition of surfactants, the vesicles from (TEG)PZnC₆₀ are thermally stable and also highly tolerant against such membrane lysis reagents.



(TEG)PZnC₆₀ was prepared by a 1,3-dipolar cycloaddition reaction involving *N*-methylglycine, C₆₀ and an aldehyde-appended *trans*-A₂BC-porphyrin zinc complex functionalized with a [G1] benzyl ether dendron bearing triethyleneglycol chains (ESI†). (TEG)PZnC₆₀ was soluble in THF, leading to a pink homogeneous solution (Fig. 1(A)), [(TEG)PZnC₆₀] = 5.0 × 10⁻² mM. On the other hand, when a THF solution of (TEG)PZnC₆₀ was added dropwise to water, a reddish brown solution resulted (Fig. 1(B)). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed the presence of uniformly sized spherical particles (Fig. 2(A) and (B)) composed of a core–shell architecture with a shell thickness of 25–30 nm (ESI†). Dynamic light scattering (DLS) analysis indicated that the vesicles are on

average 100 nm in diameter (Fig. 2(C)). From this size regime, the vesicles likely consist of a multilamellar membrane. They are highly stable against coagulation, as indicated by no change in particle size over a period of three months, even at much higher concentrations such as 0.1 mM.

UV–vis spectroscopy of an aqueous solution of the vesicles showed zinc porphyrin absorption bands at 426 (Soret), 548 and 585 (Q-bands) nm, which are red-shifted from those in THF (Fig. 1(C)). These absorption bands were also broader, and their absorption coefficients were smaller than those in THF (*e.g.*, Soret band; $\epsilon = 2.90 \times 10^5$ in THF; 1.25×10^5 L mol⁻¹ cm⁻¹ in water). Furthermore, a long tailing was observed in the near-IR region (650–1000 nm; Fig. 1(B), inset), which is characteristic of

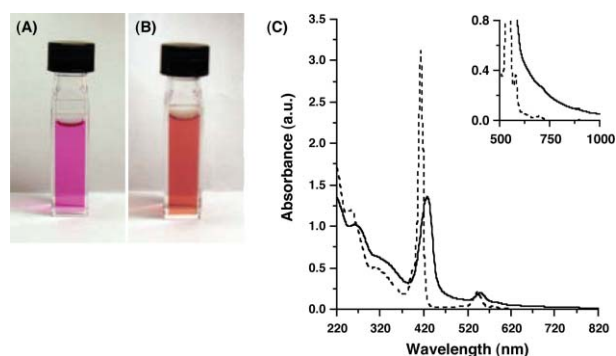


Fig. 1 Photographs of (A) THF and (B) aqueous solutions of (TEG)PZnC₆₀ at 5.0 × 10⁻² mM, and (C) their electronic absorption spectra (broken curves; THF, solid curves; water) at 1.0 × 10⁻² mM (inset; 0.1 mM).

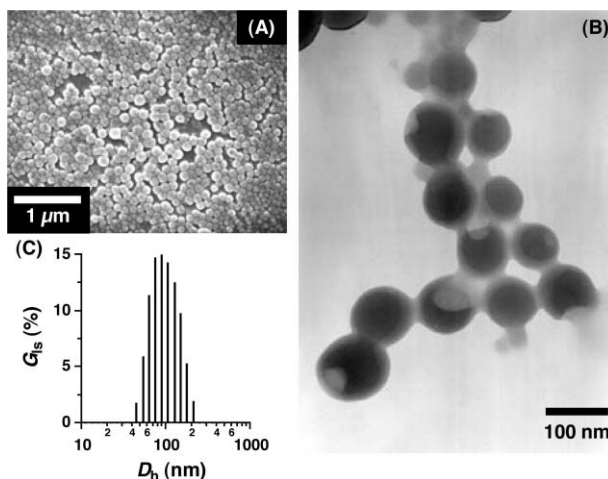


Fig. 2 (A) SEM and (B) TEM micrographs of cast samples prepared from an aqueous solution of (TEG)PZnC₆₀, and its DLS profile at [(TEG)PZnC₆₀] = 1.5 × 10⁻² mM (*I*²*G*² = 0.187).

† Electronic supplementary information (ESI) available: Details for synthesis of (TEG)PZnC₆₀, preparation of vesicles, and guest trapping and releasing experiments, Figs. S1–S9. See <http://www.rsc.org/suppdata/cc/b4/b409228g/>

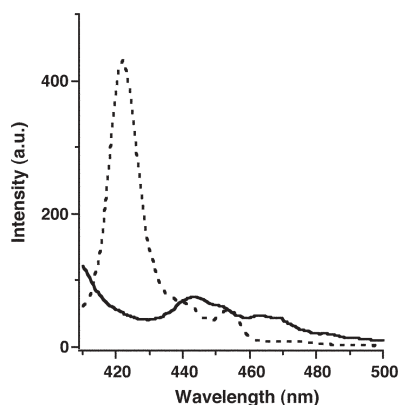


Fig. 3 S_2 emission spectra of (TEG)PZnC₆₀ ($\lambda_{\text{ext}} = 400$ nm, abs = 0.2) in THF (broken curve) and water (solid curve).

charge-transfer π -electronic interactions between zinc porphyrins and fullerenes as reported for some covalently linked⁴ or supramolecularly complexed^{3c} porphyrin and fullerene units. Therefore, it is most likely that the multilamellar vesicular membrane consisting of (TEG)PZnC₆₀ involves an interdigitating structure, in which the fullerene moieties are sandwiched by the zinc porphyrin units. As expected from this configuration, (TEG)PZnC₆₀ in the membrane displayed a quite different emission profile from non-associated (TEG)PZnC₆₀. Zinc porphyrin–fullerene dyads are known to behave as excellent intramolecular electron-transfer modules.⁵ Nevertheless, non-associated (TEG)PZnC₆₀ in THF fluoresced, to a certain extent, at 586 and 634 nm (S_1 emission) upon excitation of the zinc porphyrin unit at 543 nm (Q-band). In sharp contrast, the fluorescence was completely quenched when (TEG)PZnC₆₀ was associated in the vesicular membrane. Furthermore, the S_2 emission, observed upon excitation of the vesicles at 400 nm (Fig. 3), was red-shifted to 443 nm (solid curve) from that in THF (422 nm; broken curve) and also remarkably quenched. Such great enhancements of the fluorescence quenching, observed for the self-assembled (TEG)PZnC₆₀, indicate that the electron transfer takes place intermolecularly as well as intramolecularly in the vesicular membrane.

The vesicles consisting of (TEG)PZnC₆₀ are thermally stable, as they substantially preserved morphological and spectral characteristics when an aqueous solution of these assemblies was heated at 70 °C for 5 h (ESI†). On the other hand, the vesicles were easily disrupted upon addition of THF. By monitoring the zinc porphyrin S_1 emission which is sensitive to the aggregation of (TEG)PZnC₆₀, we investigated at 25 °C the dissociation/association events of this π -electronic amphiphile at different THF contents, and found a clear hysteresis profile as shown in Fig. 4. This is in sharp contrast with the dissociation behavior of vesicles consisting of an ionic amphiphilic fullerene without any metalloporphyrin moiety.⁶ We consider that the hysteresis profile in Fig. 4 most likely stems from the zinc porphyrin-to-fullerene charge transfer interaction in self-assembled (TEG)PZnC₆₀, which possibly stabilizes the vesicular membrane once formed.

The vesicles in their interior space can accommodate guest molecules when they are present in the self-assembling process. For example, vesicles containing sulforhodamine-G, a typical hydrophilic fluorescent probe, could be prepared and successfully isolated by Sephadex[®] G-50 gel filtration (ESI†). Quite interestingly, sulforhodamine-G, thus entrapped, did not escape from the vesicles

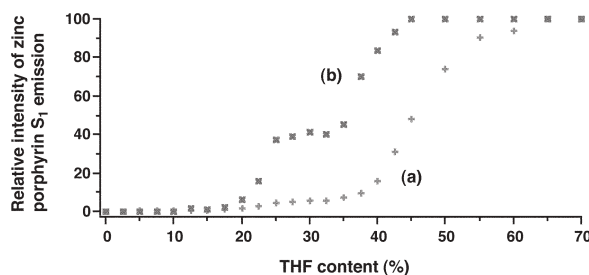


Fig. 4 Intensity changes in zinc porphyrin S_1 emission at 637 nm ($\lambda_{\text{ext}} = 414$ nm, abs = 0.15) upon addition of THF to a vesicle solution, (a) and addition of water to a THF solution of (TEG)PZnC₆₀, (b).

over a period of one month. On the other hand, upon dilution with THF, collapse of the vesicles took place, resulting in release of sulforhodamine-G, as evidenced by an enhancement in its fluorescence emission (ESI†). To our surprise, addition of a surfactant such as Triton X-100 did not trigger the release of the encapsulated dye (ESI†). Such a high stability towards detergents is remarkable, since ordinary lipid vesicles are easily disrupted upon treatment with detergents. In this sense, the vesicles from (TEG)PZnC₆₀ behave much like polymersomes, *i.e.*, vesicles from amphiphilic block copolymers.⁷

In conclusion, we have demonstrated that a novel non-ionic π -electronic amphiphile consisting of a zinc porphyrin–fullerene dyad (TEG)PZnC₆₀ self-assembles into uniformly-sized, multi-lamellar micro-vesicles in aqueous media. A metalloporphyrin-to-fullerene charge transfer interaction taking place within the multilayer membrane possibly stabilizes the vesicles and also makes them tolerant towards membrane lysis with detergents. The vesicles can retain guest molecules much longer than ordinary lipid vesicles and as such behave like polymersomes. Studies on photochemical communication between the interior and exterior spaces of the vesicles and related applications are the interesting subjects worthy of further investigation.

Notes and references

- (a) J. N. Israelachvili, D. J. Mitchell and B. W. Ninham, *J. Chem. Soc., Faraday Trans. 2*, 1976, 1525; (b) T. Kunitake, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 709.
- Tubular assemblies consisting of an ionic zinc porphyrin–fullerene amphiphilic dyad have been reported in: V. Georgakilas, F. Pellarini, M. Prato, D. M. Guldi, M. Melle-Franco and F. Zerbetto, *Proc. Nat. Acad. Sci. USA*, 2002, **99**, 5075.
- (a) K. Tashiro, T. Aida, J.-Y. Zheng, K. Kinbara, K. Saigo, S. Sakamoto and K. Yamaguchi, *J. Am. Chem. Soc.*, 1999, **121**, 9477; (b) J.-Y. Zheng, K. Tashiro, Y. Hirabayashi, K. Kinbara, K. Saigo, T. Aida, S. Sakamoto and K. Yamaguchi, *Angew. Chem., Int. Ed.*, 2001, **40**, 1857; (c) K. Tashiro and T. Aida, *J. Inclusion Phenom. Macrocycl. Chem.*, 2001, **41**, 215; (d) P. D. W. Boyd, M. C. Hodgson, C. F. E. Rickard, A. G. Oliver, L. Chaker, P. J. Brothers, R. D. Bolskar, F. S. Tham and C. A. Reed, *J. Am. Chem. Soc.*, 1999, **121**, 10487.
- N. Armaroli, G. Marconi, L. Echegoyen, J.-P. Bourgeois and F. Diederich, *Chem. Eur. J.*, 2000, **6**, 1629.
- (a) H. Imahori, K. Hagiwara, M. Aoki, T. Akiyama, S. Taniguchi, T. Okada, M. Shirakawa and Y. Sakata, *J. Am. Chem. Soc.*, 1996, **118**, 11771; (b) D. M. Guldi, *Chem. Soc. Rev.*, 2002, **31**, 22.
- G. Angelini, P. De Maria, A. Fontana, M. Pierini, M. Maggini, F. Gasparrini and G. Zappia, *Langmuir*, 2001, **17**, 6404.
- (a) D. D. Lasic, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1685; (b) D. E. Discher and A. Eisenberg, *Science*, 2002, **297**, 967; (c) M. Antonietti and S. Förster, *Adv. Mater.*, 2003, **15**, 1323.