

DESIGN AND APPLICATIONS OF SUPRAMOLECULAR PORPHYRIN/FULLERENE NANO HYBRIDS

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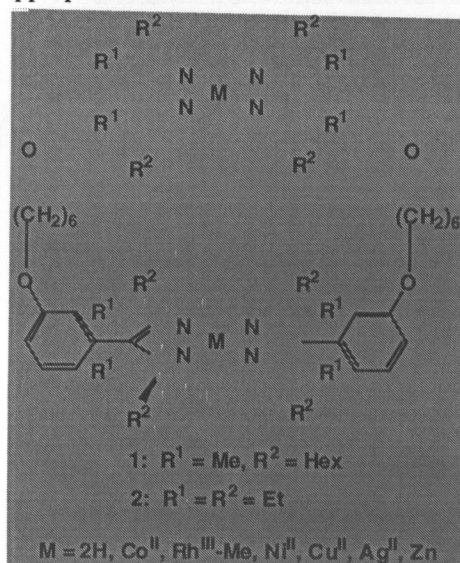
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Supramolecular complexation of fullerenes with metalloporphyrins attracts attention for the construction of electronic/magnetic devices and molecular machines, considering an interesting potential that their properties can be switched photo- and electrochemically. We have recently found that cyclic dimers of metalloporphyrins can bind fullerenes to form stable inclusion complexes [1, 2], where appropriate selection of the central metal ions of the



host molecule results in an extremely high association constant ($\sim 10^8 \text{ M}^{-1}$). For example, when a host molecule with Rh^{III} is used, exchange of included and free fullerenes is much slower than the NMR timescale [3]. X-ray crystallography and several spectroscopic profiles of an inclusion complex of C_{60} with a zinc porphyrin cyclic dimer have indicated π -electronic and charge-transfer host-guest interactions [3, 4]. More recently, we have found that a host molecule with Rh^{III} , under appropriate conditions, forms a 1:1 inclusion complex with C_{120} , in which the host molecule switches back and forth between the two carbon nano-spheres of C_{120} (supramolecular oscillator) [5]. The oscillation frequency sensitively changes with temperature. Furthermore, the oscillation properties can be tuned by the axial group on Rh^{III} . We have also found that inclusion complexes between cyclic dimers of paramagnetic metalloporphyrins and endohedral metallofullerenes display a ferromagnetic spin-spin coupling, suggesting their interesting potential as novel magnetic nano materials [6].

In conclusion, the inclusion chemistry of fullerene with cyclic oligomers of metalloporphyrins provides a new aspect in supramolecular π -electronic materials and nano

devices.

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- [1] Tashiro, K.; Aida, T.; Zheng, J. -Y.; Kinbara, K.; Saigo, K.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **1999**, *121*, 9477.
- [2] T. Nishioka, Tashiro, K.; Aida, T.; Kinbara, K.; Saigo, K.; Sakamoto, S.; Yamaguchi, *Macromolecules*, **2000**, *33*, 9182.
- [3] Zheng, J. -Y. Tashiro, K.; Hirabayashi, Y.; Kinbara, K.; Saigo, K.; Aida, T.; Sakamoto, S.; Yamaguchi, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 1857.
- [4] Tashiro, K.; Aida, T. *J. Inc. Phen.* in press.
- [5] Tashiro, K.; Hirabayashi, Y.; Aida, T.; Saigo, S.; Fujiwara, K.; Komatsu, K.; Sakamoto, S.; Yamaguchi, K. submitted.
- [6] Kato, K.; Okubo, S.; Toyama, N. Tashiro, K.; Aida, T.; Saigo, S.; Akasaka, T.; Sakamoto, S.; Yamaguchi, K. submitted.

