

seminar

Monday 23th January

c/Faraday, 9

Conference Hall

Imdea Nanociencia

Ciudad Universitaria de Cantoblanco

12:00h

New Aspects in Dipyrrin-Metal Complexes:
From Molecular Science to Low-Dimensional
Molecular Assemblies

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The present paper is devoted to my achievements in dipyrrin-metal complex chemistry for this five years.[1]. One of such examples includes heteroleptic (dissymmetric) bis(dipyrrinato)zinc(II) complexes that feature more intense luminescence than corresponding 4,4-difluoro-4-bora-3a,4a-diaza-s-indacenes (BODIPYs).[1a-f] We then expanded the concept of dissymmetry, creating dinuclear bis(dipyrrinato)zinc(II) complexes that transmit excitons quantitatively from one end to the other.[1g] Also, the concept of dissymmetry allowed us to fabricate [bis(oxazoline)](dipyrrinato)zinc(II) complexes that feature bright and circularly polarized luminescence from an originally achiral dipyrrinato ligand.[1h] Taking advantage of the spontaneous coordination reaction between dipyrrin and metal ions, we created two types of photofunctional molecular superstructures. A liquid/liquid interfacial reaction between a bridging dipyrrin ligand and metal(II) ions gives rise to single crystals of a onedimensional coordination polymer suitable for X-ray diffraction analysis. Isolated single fibers of the zinc coordination polymer may be exfoliated from the single crystal or bulk solid upon ultrasonication. Atomic force microscopy detects the isolated fibers with lengths of more than several μm . The exfoliated wire features good processability, realizing a thin film on a transparent SnO₂ electrode. The modified SnO₂ electrode serves as a photoanode for a photoelectric conversion system.[1i,j] Although molecule-based bottom-up nanosheets manufactured directly from molecular components can exhibit greater structural diversity than top-down nanosheets, the bottom-up nanosheets reported thus far lack useful functionalities. Here we show the design and synthesis of a bottom-up nanosheet featuring a photoactive bis(dipyrrinato)zinc(II) complex motif (Fig. 1). A liquid/liquid interfacial synthesis between a three-way dipyrrin ligand and zinc(II) ions results in a multi-layer nanosheet, whereas an air/liquid interfacial reaction produces a single layer or few-layer nanosheet with domain sizes of $>10 \mu\text{m}$. The bis(dipyrrinato)zinc(II) metal complex nanosheet is easy to deposit on various substrates using the Langmuir-Schäfer process. The nanosheet deposited on a transparent SnO₂ electrode functions as a photoanode in a photoelectric conversion system and is thus the first photofunctional bottom-up nanosheet.[1k-m]

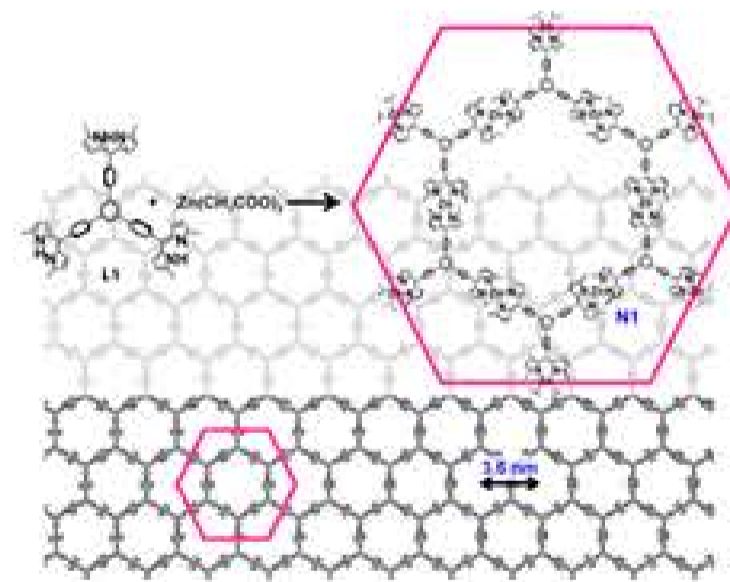


Fig. 1 Bis(dipyrrinato)zinc(II) complex nanosheet.

references

- [1] (a) *J. Am. Chem. Soc.* **2016**, *138*, 5666. (b) *Dalton Trans.* **2015**, *44*, 15103. (c) *Inorg. Chem.* **2014**, *53*, 3275. (d) *Molecules*, **2013**, *18*, 4090. (e) *Dalton Trans.* **2012**, *41*, 14035. (f) *Chem. Asian J.* **2012**, *7*, 907. (g) *Chem. Commun.* **2014**, *50*, 5881. (h) *Angew. Chem. Int. Ed.* **2016**, *55*, 1377. (i) *Chem. Sci.* **2015**, *6*, 2853. (j) *J. Mater. Chem. A* **2015**, *3*, 15357. (k) *Nat. Commun.* **2015**, *6*, 6713. (l) *Coord. Chem. Rev.* **2016**, doi:10.1016/j.ccr.2015.12.001. (m) *Langmuir* **2016**, *32*, 2527. (n) *Inorg. Chem.* **2016**, *10.1021/acs.inorgchem.6b00431*. (o) *Chem. Asian J.* **2013**, *8*, 723. (p) *Electrochemistry*, **2013**, *81*, 337.

Nanociencia y Nanotecnología: lo pequeño es diferente

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