

Macrocyclic Aromatic Ether-Imide-Sulfones: Versatile Supramolecular Receptors with Extreme Thermochemical and Oxidative Stability

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Over the past two decades there has been an explosion of interest in the design and synthesis of molecular receptors,¹ including those which exploit donor–acceptor interactions between aromatic π -systems² to direct, for example, the synthesis of catenanes and rotaxanes.³ This latter chemistry has enabled the fabrication of nanoscale devices including light- and redox-driven switches⁴ and most recently molecular logic-gates.⁵ However, the components of such systems have generally involved rather labile substructures such as *N*-benzylbipyridinium units⁶ or *N*-alkynyl-methylene-imide linkages,⁷ and it seems probable that much more chemically robust systems will be needed for molecular computing to be developed into a fully practicable technology. Recognizing that *all-aromatic* polyimides and polysulfones are among the most stable of all organic materials,⁸ we have investigated the synthesis of macrocyclic analogues of such polymers and here report that macrocycles of this type are both readily obtained and show considerable versatility as supramolecular receptors.

Direct [1 + 1] cyclocondensation of diamine **1** with pyromellitic dianhydride (**2**) or 1,4,5,8-naphthalenetetracarboxylic dianhydride (**3**) in refluxing dimethylacetamide, under pseudohigh dilution conditions, gave the macrocyclic aromatic imide-sulfones **4** and **5** in 23 and 20% yields, respectively (Chart 1). These macrocycles have extremely high but still clearly observable melting points (sharp DSC endotherms at 493 and 547 °C, respectively) and show no evidence for thermo-oxidative decomposition in air at temperatures up to 400 °C (see Supporting Information).

Addition of the π -electron donor molecules pyrene, perylene, 2,6-dimethoxynaphthalene, tetrathiafulvalene, and pyren-1-ol to solutions of the almost colorless **4** and **5** produced intense colors assigned to intermolecular charge-transfer absorptions, and ¹H NMR spectra for equimolar ratios of receptor to substrate showed large ring-current-induced complexation shifts (up to 1.5 ppm; see Supporting Information Figures 1 and 2). Binding constants for macrocycle **5** with different substrates were determined by UV–visible spectroscopy in chloroform–hexafluoro-2-propanol (6:1 v/v) using the dilution technique and gave values ranging from 40 M^{−1} for 2,6-dimethoxynaphthalene, to 800 M^{−1} for pyrene, 1400 M^{−1} for perylene, and 2300 M^{−1} for 1-hydroxypyrene. A Job plot confirmed the stoichiometry of complex formation in solution between **5** and pyrene to be 1:1. Dark green crystals of a 1:1 complex (**6**) between **5** and perylene were isolated from solution in dimethylformamide by vapor diffusion with diethyl ether, and single-crystal X-ray analysis showed the perylene molecule to be inserted almost symmetrically into the macrocyclic cavity (Figure 1). Distances between the center of the perylene molecule and the

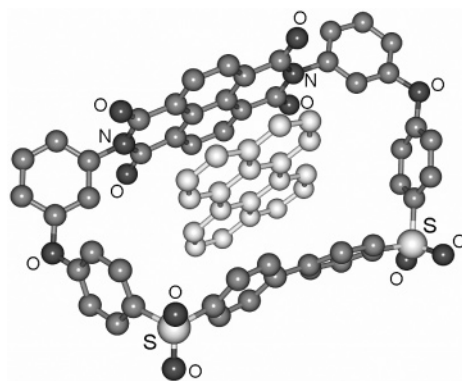
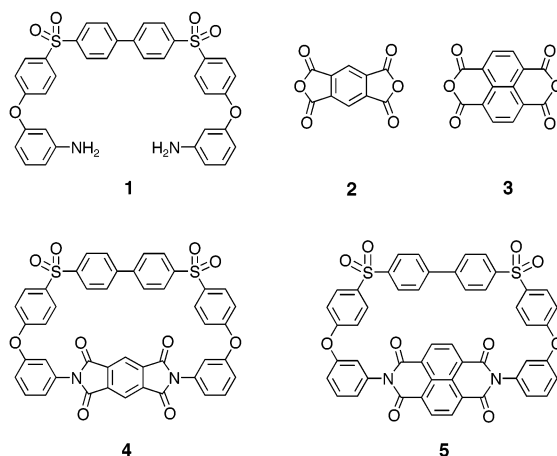


Figure 1. X-ray structure of the 1:1 complex (**6**) formed between macrocycle **5** and perylene.

Chart 1



centers of the biphenyl linkage and diimide ring system are 3.57 and 3.51 Å, respectively, and the vectors linking these centers are essentially collinear (179°). Notably, the transannular separation between the centers of the biphenyldisulfonyl and diimide units in complex **6** is only 7.08 Å, a very significant (~14%) contraction from the value of 8.19 Å observed for the “pure” macrocycle which contains only dichloromethane of solvation. Complexation evidently induces the receptor to flex substantially to optimize the fit with its substrate (Supporting Information, Figure 3).

Transition metal derivatives of 8-hydroxyquinoline have long been known to act as π -donor molecules in conventional “charge-transfer” complexes.⁹ In the present work, we have shown that addition of bis(8-quinolinolato)palladium(II) to a solution of macrocycle **5** in chloroform leads to rapid crystallization of a complex (**7**) having 2:1 (host:guest) stoichiometry. Remarkably, this complex can also be obtained in essentially quantitative yield

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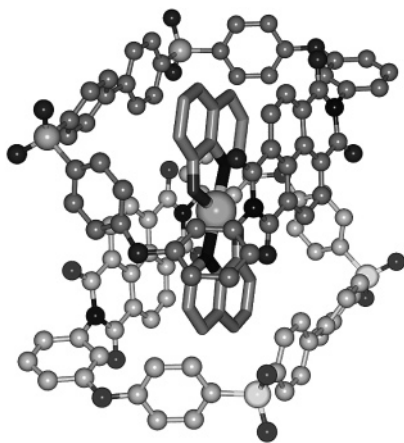


Figure 2. X-ray structure of the 1:2 complex (**7**) formed between bis(8-quinolinolato)palladium(II) and macrocycle **5**.

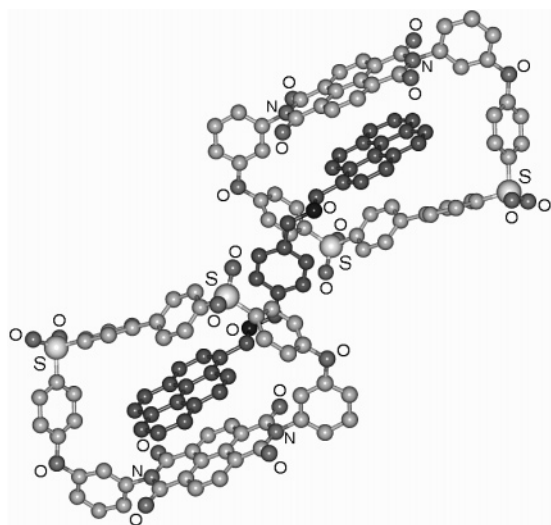


Figure 3. X-ray structure of the [3]pseudorotaxane (**8**) formed between α,α -bis(1-pyrenylmethoxy)-1,4-xylene and macrocycle **5**.

from a solution containing stoichiometric quantities of palladium(II) acetate, 8-hydroxyquinoline, and macrocycle **5**, simply by adding triethylamine to deprotonate the ligand. Single-crystal X-ray analysis shows that complex **7** is in fact a [3]pseudorotaxane (Figure 2), with a macrocycle complexed to each of the two quinolinolato(1-) ligands.

In complex **7**, the two macrocycles are related by a crystallographic inversion center at palladium. The oxyquinoline ring system π -stacks with the macrocycle in a rather different fashion to that of the perylene molecule in **6**, interacting mainly with the naphthalenetetracarboximide residue (interplanar separation 3.46 Å) and having little geometric overlap with the biphenylene unit (closest approach 4.00 Å). Double-encirclement of a central "thread" is also demonstrated in the [3]pseudorotaxane **8** (Figure 3), whereby two pyrene ring systems, linked by a 1,4-xylenyldi(oxyethylene) spacer, interact with two molecules of **5**. The π - π stacking interactions involve both imide and biphenylenedisulfone residues,

although here again the imide unit approaches the substrate rather more closely than does the biphenylene fragment (centroid-centroid separations are 3.66 and 3.91 Å, respectively). It is significant that, in the corresponding perylene complex **6**, much closer contact (3.57 Å) between the biphenylene-disulfone unit and the substrate results in a considerable flattening of the torsion angle about the biaryl linkage (19° in **6**, 30° in **7**, and 42° in **8**).

Receptors **4** and **5** and their complexes represent only prototype structures for an entire new family of self-assembling molecular architectures with very high thermochemical stability. In view of their ready accessibility (see Supporting Information), robust chemical nature, and evident versatility in complexation, receptors of this type clearly have the potential to become "workhorse" molecules in the future development of supramolecular chemistry.

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Supporting Information Available: Synthetic procedures, spectroscopic analyses, and thermo-oxidative stabilities for macrocycles **4** and **5**; proton NMR data for complexation of **4** with pyrene and of **5** with pyren-1-ol; synthesis of the metallo-[3]pseudorotaxane **7** (PDF); full crystallographic data for **4**, **5**, **6**, **7**, and **8** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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