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Enhanced fluorescence quenching in receptor-containing conjugated polymers: a calix[4]arene-containing poly(phenylene ethynylene)†

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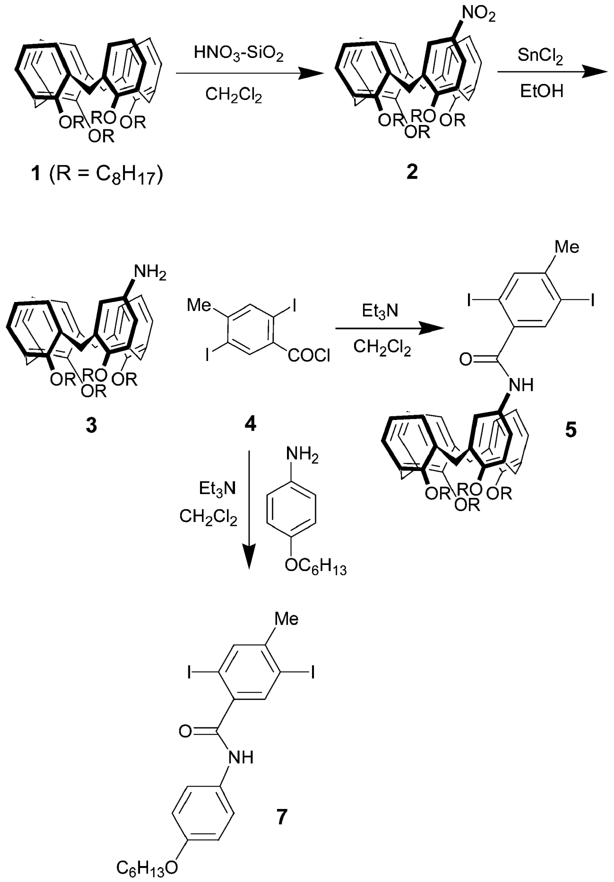
A fluorescent poly(phenylene ethynylene) containing calix[4]arene-based receptor units has a sensitivity to quenching by the *N*-methylquinolinium ion that is over three times larger than that seen in a control polymer lacking calix[4]arenes.

Previous research by our group and others has established the utility of semiconductive conjugated organic polymers in the creation of sensors with unparalleled sensitivity.[1] Exciton migration in these materials provides an amplification mechanism in which electron- or energy-transfer effects arising from trace amounts of small-molecule quenchers come to dominate the fluorescence properties of the conjugated polymer. Following this principle, electron transfer from or to excited conjugated polymers has been applied to the detection of redox-active analytes such as methylviologen,[2] trinitrotoluene (TNT),[3] electron-rich aromatics,[4] and Fe^{3+}-containing proteins.[5] High analyte sensitivity in these systems is provided by strong static polymer–quencher binding, which overcomes the inefficiency of collisional (dynamic) quenching for materials with short excited-state fluorescence lifetimes. In many cases, these static quenching effects arise from non-specific (generally electrostatic) interactions between the polymer and quencher, a fact which necessarily limits the specificity of proposed analytical schemes. Additionally, the requirement for strong analyte binding limits the applicability of polymer-amplified systems to the detection of quenchers in which the analyte and polymer backbone have a strong inherent interaction.

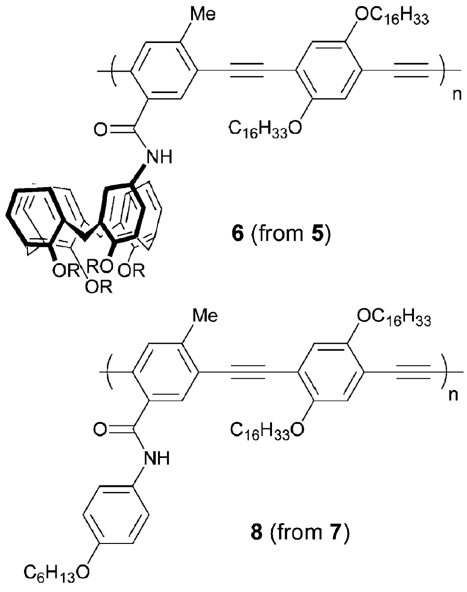
Improvements in the analytical utility of conjugated polymer-based sensors will require innovations in polymer design that take advantage of specific supramolecular interactions to detect specific analytes of interest. Towards this end, we have sought to introduce known receptor units into a poly(phenylene ethynylene) (PPE) to provide binding sites for a target analyte of interest. As a demonstration, we have made use of the calix[4]arene skeleton to construct a host for the electron-poor, fluorescence-quenching *N*-methylquinolinium (NMQ) ion. Calixarenes have long been recognized as versatile supramolecular scaffolds for a number of applications in organic chemistry and materials science, and procedures for the selective functionalization of the calix[4]arene core have been worked out in detail.[6] In particular, the exhaustive substitution of the phenolic 'lower rim' of calix[4]arenes with long alkyl groups under certain conditions provides structures locked in the 'cone' conformation, which has been shown to weakly bind substituted *N*-methylpyridinium cations ($K_a \sim 5\ M^{-1}$).[7] Ligand binding in these systems is thought to arise through co-operative cation–π interactions between the highly π-basic calixarene cavity and the relatively π-electron-poor guest cations. We reasoned that a PPE incorporating these cone calix[4]arene host units would show enhanced quenching by the closely related *N*-methylquinolinium ion.

The synthesis of the cone calix[4]arene PPE monomer **5** was carried out according to the sequence shown in Scheme 1.

Nitration of calix[4]arene tetraoctyl ether **1**[8] with silica-supported



Scheme 1 Synthesis of monomers **5** and **7**.



Scheme 2 Structures of polymers **6** and **8**.

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† Electronic supplementary information (ESI) available: synthetic conditions; fluorescence studies. See http://www.rsc.org/suppdata/cc/b4/b411489b/

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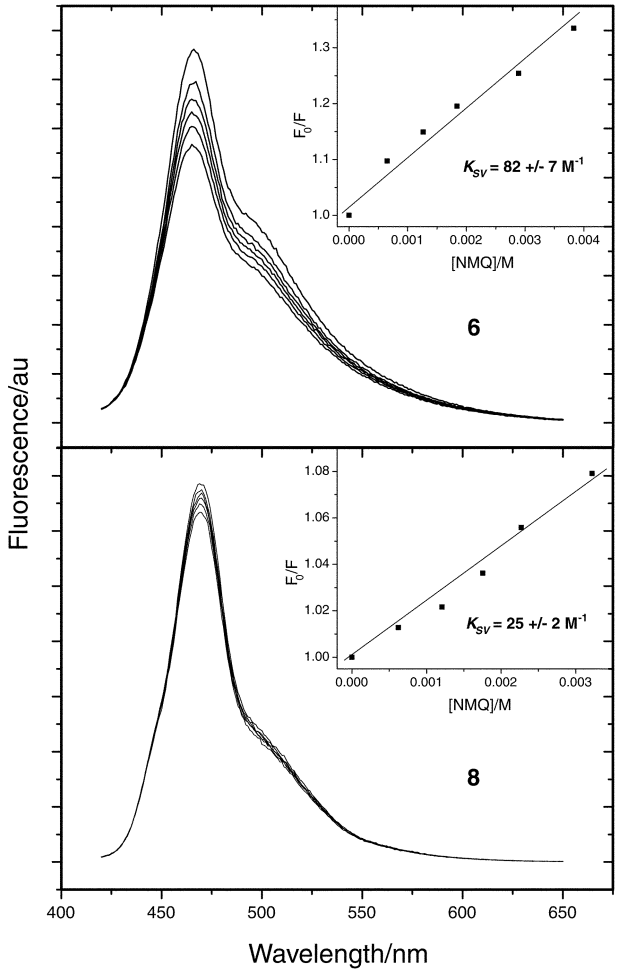
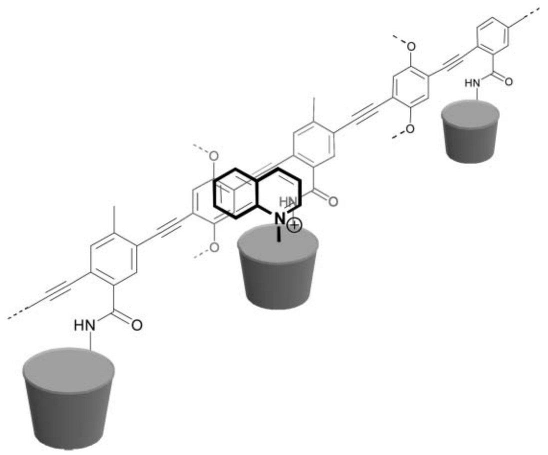


Fig. 1 Fluorescence spectra of **6** (top) and **8** (bottom) on treatment with increasing quantities of *N*-methylquinolinium (NMQ) hexafluorophosphate, with corresponding Stern–Volmer plots (insets). Fluorescence traces represent NMQ concentrations as follows: for **6**, top to bottom: 0 mM, 0.65 mM, 1.3 mM, 1.8 mM, 2.9 mM, 3.8 mM. For **8**, top to bottom: 0 mM, 0.62 mM, 1.2 mM, 1.8 mM, 2.3 mM, 3.2 mM.

nitric acid in dichloromethane provided a mixture of nitrocalix[4]-arenes from which the mono-nitro compound **2** could be isolated in good yield. Reduction of **2** with $SnCl_2$ in ethanol provided the calix-aniline **3** which was condensed with the acid chloride **4**[2] to provide monomer **5**. Compounds **2**, **3** and **5** all show ^{1}H NMR spectra consistent with mono-substituted calix[4]arenes locked in the cone conformation. Separately, a 4-hexyloxyphenyl-substituted monomer **7** was synthesized to provide a non-calixarene mimic of the electronic environment provided by **5**. Co-polymerization of **5** and **7** with 2,5-diethynyl-1,4-bis(hexadecyloxy)benzene provided polymers **6** and **8** (Scheme 2) as yellow-orange solids of comparable molecular weight (**6**: M_n = 14 000, PDI = 1.8; **8**: M_n = 7 900, PDI = 1.4).

We made use of the Stern–Volmer equation $F_0/F = 1 + K_{SV}[Q]$ to determine the relative degree of quenching of **6** and **8** as a function of NMQ concentration. In dichloromethane solution, **6** is quenched by the hexafluorophosphate salt of NMQ with a K_{SV} of 82 ± 7 M^{-1}, relative to 25 ± 2 M^{-1} for the control polymer **8** (Fig. 1). Furthermore, we observed that the fluorescence lifetimes of these polymers remained unchanged (at 0.55 ± 0.02 ns) at all quencher concentrations, suggesting that the formation of ground-state, statically quenched polymer–quencher complexes dominates the fluorescence quenching mechanism in these systems. As a result, the greater than threefold enhancement in K_{SV} provided by the use of pendant cone calix[4]arene units stems from enhanced binding of the NMQ ion by the calix[4]arene receptors. On this basis, we propose that the effects of the electron-rich polymer backbone and the π-basic calix[4]arene cavity act synergistically to provide a stronger overall binding effect (manifested as a larger static K_{SV}) than that seen when the calix[4]arene units are absent (Scheme 3).



Scheme 3 Schematic diagram of the NMQ ion binding to polymer **6**.

The weak-binding calix[4]arene units present in polymer **6** are able to produce such a large quenching enhancement has implications for the design of specific and reversible fluorescent sensors based on host–guest interactions. We are currently exploring techniques to apply these principles to polymer systems in which host–guest interactions enhance quenching or energy transfer effects with related small molecules.

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