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Hyperconjugative and Inductive Perturbations in Poly(*p*-phenylene vinylenes)

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Poly(*p*-phenylene vinylene) (PPV) and its derivatives are among the most extensively studied organic semiconductive polymers. Despite their processablity, high luminescence, and structural diversity, several challenges remain for further applications. As in many conjugated polymers (CPs), the fluorescence quantum yields of PPVs are substantially lower in the solid state due to interchain interations.[1] Successful approaches to enhance the solid-state emission efficiency of CPs include the incorporation of bulky side chains or rigid three-dimensional moieties.[2] Another key issue to be addressed is the tuning of the electron affinity of CPs to control their work functions and charge transporting properties.[3] Traditionally, atoms with lone pair electrons capable of electron-donating or electronegative groups connected directly to the π-system have been utilized to modify their electron affinity. Although direct attachment of such groups can produce large effects, steric repulsion of bulky substituents at the phenylene or vinylene subunits often induce deviations from planarity and decrease conjugation.[4]

We are interested in developing new CP designs that produce high fluorescence quantum yields and also tune electron affinity. Simultaneously, we seek architectures for the covalent attachment of the CPs to peptides, nucleic acids, or antibodies for biosensor applications that avoid potentially deleterious barriers or traps[5] in the electronic structure caused by conformational disorder. Herein, we report novel CPs having three-dimensional structures that display highly efficient solid-state fluorescence and demonstrate how groups with hyperconjugation and inductive interactions can be used to tune their electron affinity.

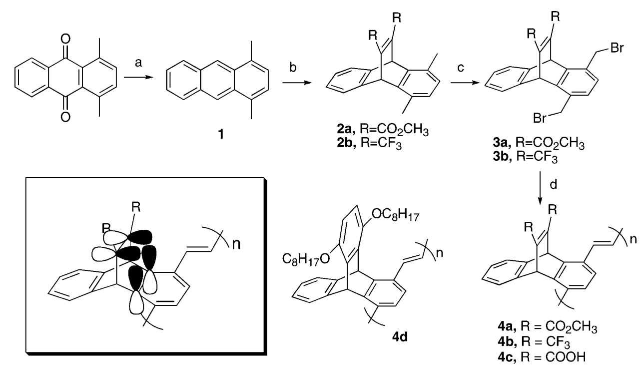
To perturb the electronic structure of CPs without interrupting conjugation by adding steric bulk in the plane of polymer backbone, we designed a new [2.2.2] bicyclic ring system that contains an electron-deficient double bond that can interact with the polymer backbone in a hyperconjugative fashion (Scheme 1).[6] Compounds **3a** and **3b**, which have ester or trifluoromethyl groups appended to the alkene of the bicyclic ring system, were synthesized and then polymerized by reaction with excess KO^{t}Bu to give polymers **4a** and **4b** (Scheme 1). Ester groups in polymer **4a** included both methyl and (30%) *tert*-butyl groups, with the latter being produced by transesterification under the polymerization conditions. The triptycene polymer **4d** represents an electron-rich model polymer for the comparison with relative electron-poor polymers **4a** and **4b**. The absorption and emission maxima of polymers **4a** and **4b** are extremely similar (Table 1). The insensitivity of **4a**'s spectra to partial transesterfication with *tert*-butyloxy groups confirms that the [2.2.2] system tolerates bulky groups without reducting conjugation length. High fluorescence quantum yields were observed for all of the polymers in THF solution and in thin films. The latter feature is attributed to the greatly reduced interchain interactions enforced by the three-dimensional frameworks.[1]

The effect of hyperconjugative perturbations on the sensory properties was determined by investigating fluorescence quenching responses of thin films with exposure to vapors of electron-rich (*N*,*N*-dimethyl *p*-toluidine (DMT)) and electron-deficient (2,4-dinitrotoluene (DNT)) aromatic compounds. All of thin films displayed the largest quenching response (Figure 1) to DNT despite the fact that it has lower vapor pressure (1.47×10^{-4} mmHg) than DMT (1.78×10^{-1} mmHg). This result is likely due to the former's strong π-acid character that favors association with electron-donating π-electron systems.[2] As shown in Figure 1 the relative quenching response of **4a**, **4b**, and **4d** reflects the expected hyperconjugative and inductive effects with **4b** being the most oxidizing and **4d** being the most reducing.[7] Hence, **4b** gives the strongest relative response to DMT and the weakest relative response to DNT. Correspondingly, **4d** displays the opposite behavior having a larger response relative to that of the other polymers to DNT and a weaker relative response to DMT. Polymer **4a** exhibits responses intermediate to those of **4b** and **4d**.

To further investigate the quenching behavior, we conducted solution Stern−Volmer quenching studies and determined the rates of static and dynamic quenching by performing steady-state and time-resolved experiments (Figure 2).[8] Static quenching, involving a preformed complex, does not reduce the excited-state lifetime, whereas dynamic quenching, resulting from diffusion, lowers the lifetime.

The trends in the solution Stern−Volmer rate constants, summarized in Table 2, contrast markedly to those from our thin film

Scheme 1 [a]



[a] (a) $NaBH_4$, 2-propanol, reflux. (b) dimethylacetylenedicaboxylate or hexafluoroacetylene, xylene, 140 °C. (c) NBS, AIBN, CCl_4, reflux. (d) KO^{t}Bu, THF, rt.

Table 1. Summary of Molecular Weight and Photophysical Data

polymer	GPC (M_n)	PDI	Abs λ_{max} (nm) (log ϵ)	em λ_{max} (nm)	Φ_F	τ (ns)
4a (THF)	1.2×10^5	2.5	401 (3.83)	473, 498	0.58	1.16
4a (film)			401	507	0.42	
4b (THF)	6.8×10^4	2.6	403 (3.48)	471, 497	0.86	0.75
4b (film)			405	506	0.43	
4d (THF)	7.9×10^5	2.1	413 (4.32)	469, 499	0.76	0.62
4d (film)			414	477, 511	0.61	

10.1021/ja038472b CCC: $27.50

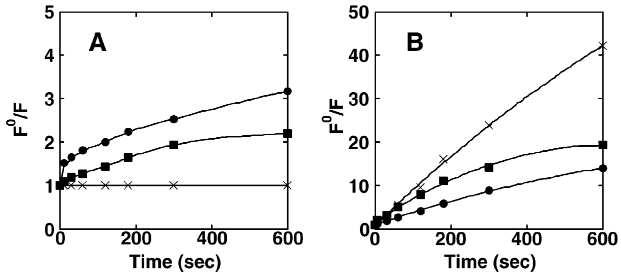


Figure 1. Stern–Volmer plots of polymers **4a** (■), **4b** (●), and **4d** (×) in spin-cast films with DMT (A) and DNT (B) vapor.

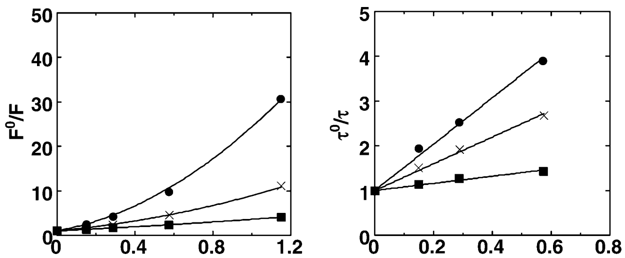


Figure 2. Stern–Volmer plots of polymers **4a** (■), **4b** (●), and **4d** (×) with *N,N*-dimethyl *p*-toluidine (DMT) in THF. The lifetime measurements are shown in the inset.

Table 2. Quenching Constants of Polymers **4a**, **4b**, and **4d**[a]

polymer	quencher	K_D (M^{-1})	K_S (M^{-1})	k_q (M^{-1} s^{-1})
4a	DMT	0.80	0.92 ± 0.58	6.9×10^8
4b	DMT	5.19	2.49 ± 0.60	7.0×10^9
4d	DMT	2.99	0.94 ± 0.67	4.8×10^9
4a	DNT	11.00	86 ± 65	9.4×10^9
4b	DNT	7.60	108 ± 93	1.0×10^{10}
4d	DNT	8.00	25 ± 15	1.3×10^{10}

[a] See Supporting Information for details of experimental conditions. (K_D, K_S, *and* k_q: Stern–Volmer quenching constant for dynamic, static quenching, and bimolecular quenching constant, respectively).

studies. As expected the electron-poor polymer **4b** exhibits the largest quenching (both static and dynamic) with DMT (Figure 2). However, we find that polymer **4d**, the most electron-rich polymer, has a much higher diffusive quenching rate than diester containing **4a** and a shorter excited-state lifetime. The deviations from thin film behaviors are even more pronounced with DNT quenching. In this case **4d** exhibits the lowest static quenching (K_s) even though it has the best sensitivity in thin films. These results underscore the fact that the sensory behaviors of conjugated polymers in solution can be very different than their responses in devices that often employ thin films. There are multiple origins for these differences including different hydrodynamic volumes for each polymer that can be influenced by the analyte, steric effects that restrict the close approach of quenchers, and the degree of amplification by energy migration. For **4d** its lower than expected solution sensitivity to DNT is likely due to the steric bulk of its alkyl side chains, and as a result it exhibits smaller static quenching than **4a** and **4b** even though it should be a better π-base.[2]

Emerging sensor applications of CPs require conjugation to biorecognition elements,[9] and to this end we have tested the acid stability of polymers **4a, 4b**, and **4d** to conditions associated with solid-phase peptide synthesis.[10] Polymer **4c** is best prepared from **4a** by treatment with aqueous acid and THF. Conjugated polymers often exhibit reactivity with strong electrophiles such as trifluoroacetic acid (TFA); however, exposure of **4b** and **4d** in CH_2Cl_2 solutions of TFA or immersion of solids in neat TFA results in no apparent reduction/modification of their emissions. Methylene chloride solutions **4a** are quenched with the addition of TFA; however, its fluorescence was immediately and completely recovered without any spectral shift after neutralization with pyridine.

In summary, we have synthesized three-dimensional polymers that have novel structures and hyperconjugative/inductive electronic perturbations. The differences in the solution and thin film sensory responses of these polymers reveal the complexities associated with any comparison of quenching sensitivities. This latter point can be dramatically illustrated wherein comparisons of sensitivities of poly(phenylene ethynylene)s and polysiloles to TNT have been found to be the same order of magnitude in solution;[11] however, thin films[2] of poly(phenylene ethynylene)s exhibit orders-of-magnitude more sensitive responses.[12]

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Supporting Information Available: Experimental procedures and photophysical study data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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