Dynamic Quenching of 5-(2′-Ethyl-hexyloxy)-*p*-Phenylene Vinylene (MEH-PPV) by Charge Transfer to a C_{60} Derivative in Solution

JIAN WANG, DELI WANG, DANIEL MOSES, ALAN J. HEEGER

Institute for Polymers and Organic Solids, University of California at Santa Barbara, Santa Barbara, California 93106-5090

ABSTRACT: The fluorescence of 5-(2′-ethyl-hexyloxy)-*p*-phenylene vinylene (MEH-PPV) quenched in solution in 1,2-dichlorobenzene by a soluble derivative of C_{60} [1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C_{61}; [6,6]PCBM] is studied by changing the concentration of the quencher and by varying the temperature. For MEH-PPV and PCBM dissolved in 1,2-dichlorobenzene, the Stern–Volmer constant (K_{SV}) is $2 \times 10^3 M^{-1}$. At high temperature, K_{SV} is enhanced because thermal energy facilitates the diffusion of PCBM. The results show that dynamic quenching (rather than static quenching) is the basic mechanism. Comparison with data obtained from quenching studies of *trans*-stilbene indicates that a single acceptor in contact with an MEH-PPV macromolecule quenches the luminescence from hundreds of repeat units. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2553–2557, 2001

Key words: fluorescence quenching; Stern–Volmer constant; photoinduced charge transfer; temperature profile

INTRODUCTION

Photoinduced electron transfer from conjugated polymers to C_{60} and its soluble derivatives has been extensively investigated[1–3] because of interest in the basic photophysics and photochemistry and because of the possibility of utilizing photoinduced charge separation to create novel materials for use in photovoltaic cells[4] and photodetector applications.[5] Because the forward electron transfer process occurs in the sub-picosecond time domain, faster than any competing process,[6,7] the quantum efficiency for charge transfer and charge

separation approaches unity. Consequently, charge transfer quenches the photoluminescence of the conjugated polymer. Although efficient charge separation occurs in the solid state only near a heterojunction interface between the polymer and the C_{60},[8] bicontinuous interpenetrating network formation at length scales in the nanometer regime result in 'bulk heterojunction' materials in which any absorbing chromophore is within a few nanometers of a heterojunction.[4]

The recent discovery of more than a million-fold amplification of the sensitivity to fluorescence quenching through photoinduced charge transfer in aqueous solution by Chen et al.[9] demonstrates a new opportunity for conjugated polymers in biological and chemical sensors for use in medical diagnostics and toxicology.[10] Inspired by the work of Chen et al., the mechanism of photoinduced charge transfer in aqueous solution has been carefully studied[11] with the conclusion that a

weakly bound complex is formed between a charged (polyanionic) conjugated macromolecule and a charged (cationic) electron acceptor, with Coulomb binding energy of $\sim$ 150 meV. In this paper, we report on photoluminescence quenching of a conjugated polymer by a soluble derivative of C_{60} in solution in an organic solvent where neither the polymer nor the acceptor is charged.

Although almost all previous studies on the physical or chemical properties of charge transfer from conjugated polymers to C_{60} were carried out in the solid state, initial measurements of the Stern–Volmer constant (K_{SV}) were reported by Zheng et al. in 1997.[12] We have expanded on their work, including both spectroscopic and temperature dependence measurements carried out on poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-p-phenylene vinylene] (MEH-PPV) and 1-(3-methoxycarbonyl)-propyl-1-phenyl[6,6]C_{61} ([6,6]PCBM)[13] in solution in 1,2-dichlorobenzene. At room temperature, $K_{SV} \approx 2 \times 10^3 M^{-1}$; at high temperatures, K_{SV} is enhanced because thermal energy facilitates the diffusion of PCBM. The results show that dynamic quenching (rather than static quenching) is the basic mechanism.

EXPERIMENTS

The MEH-PPV used in this study was obtained from UNIAX Corporation; the PCBM was supplied by Prof. F. Wudl (Chemistry Department, UCLA). The solvent, 99% anhydrous 1,2-dichlorobenzene packaged under nitrogen in Sure/Seal bottles, was purchased from Aldrich Chemical Company. The solutions were made inside a controlled atmosphere dry box by diluting a stock solution to the desired concentration. The molecular structures of MEH-PPV and PCBM are illustrated in the inset of Figure 1. The absorption spectra were obtained with a SHIMADZU UV-2401PC spectrophotometer. The 457.9 nm emission line from an Argon laser was used as the excitation source for fluorescence intensity measurements. A detailed description of the instruments and experimental techniques can be found in our previous publication.[11]

RESULTS AND DISCUSSION

Fluorescence quenching processes in solution fall into two general types[14,15]: (1) static quenching through the formation of a ground state complex;
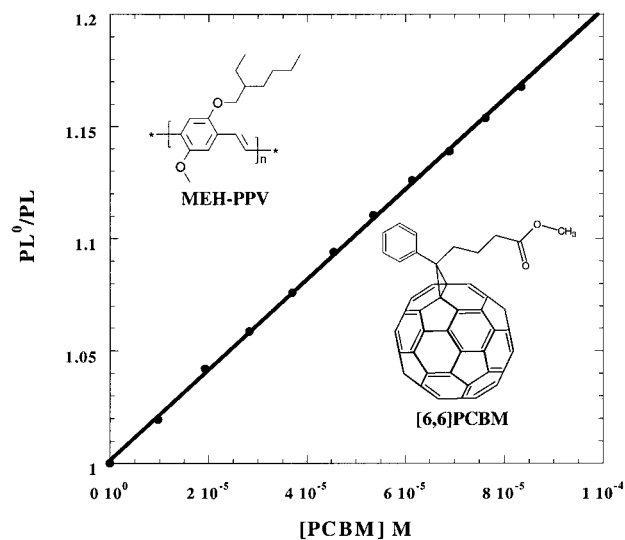

Figure 1   Stern–Volmer plot (PL of MEH-PPV over the PL of polymer with PCBM versus the PCBM concentration) from 5×10^{-6} to $1 \times 10^{-4} M$. The solid line is the fit obtained from the Stern–Volmer equation (eq. 1). The concentration of MEH-PPV is $1 \times 10^{-4 M}$. Inset: The chemical structures of MEH-PPV and PCBM.

and (2) dynamic quenching due to diffusive collisions between the photoluminescence (PL) emitter and the quencher. At low quencher concentrations, the dependences of fluorescence quenching on the quencher concentration for the two processes are identical and can be quantitatively described by the Stern–Volmer equation:

$$\frac{PL^0}{PL} = 1 + K_{SV}[\text{quencher}] \qquad (1)$$

where the PL^0 is the intensity of fluorescence in the absence of the quencher, PL is the intensity of fluorescence in the presence of the quencher and [quencher] denotes the quencher concentration (in this case, PCBM). The Stern–Volmer constant, K_{SV}, provides a quantitative measure of the quenching. In static quenching, K_{SV} is the association constant for complex formation, which is:

$$K_{SV}^S = \frac{[FQ]}{[F][Q]} \qquad (2)$$

where [FQ], [F] and [Q] are the concentrations of complex, fluorophore, and quencher, respectively. In dynamic quenching, K_{SV} is related to the diffusion-controlled bimolecular rate constant k_d and the intrinsic fluorescence lifetime τ_0[15]:

$$K_{SV}^{D} = k_d \tau_0 \qquad (3)$$

Equations 2 and 3 demonstrate clear differences between two quenching processes. For example, dynamic quenching is expected to be more effective at elevated temperatures (due to increased rate of diffusion), whereas static quenching will become less effective at elevated temperatures (due to thermal dissociation of the complex).

The fluorescence set-up was arranged in such a way that the "filter effect" due to the absorption of PCBM was <6% even at the highest PCBM concentration. Nevertheless, to account for the small absorption of PCBM at the excitation and emission wavelength of MEH-PPV, the following equation was used to correct the fluorescence intensity[12]:

$$PL = PL_{em} \times \frac{(1 - e^{-\alpha_1 C_1 d_1})}{\alpha_1 C_1 d_1}$$
$$\times \frac{\alpha_1 C_1 d_1 + \alpha_2 C_2 d_1}{(1 - e^{-(\alpha_1 C_1 d_1 + \alpha_2 C_2 d_1)})} \times e^{\alpha_3 C_2 d_2} \quad (4)$$

where PL_{em} is the experimental fluorescence intensity; PL is the corrected fluorescence intensity; α_1, C_1, and α_2, C_2 are the absorption coefficients and concentrations of MEH-PPV and PCBM, respectively, at the excitation wavelength; α_3 is the absorption coefficient of PCBM at emission wavelength of MEH-PPV (560 nm); d_1 is the slit width in the emission measurement; and d_2 is the distance which the emitted light traveled in the solution before reaching the detector. Because the fluorescence was detected at 90 degrees to the incident laser beam, d_2 is precisely defined (see ref. 14).

A Stern–Volmer plot of the PL quenching of MEH-PPV by PCBM is shown in Figure 1. The data points shown in the Figure 1 have been corrected for PCBM absorption using eq. 4. The dependence on quencher concentration is linear with $K_{SV} \approx 2 \times 10^3 M^{-1}$, which is consistent with the result reported by Zheng et al.[12]

From eqs. 2 and 3, it is clear that the PL quenching data alone cannot distinguish between dynamic or static processes. Additional information is required to distinguish between the two; for example, absorption spectra and the temperature dependence of K_{SV}.[15]

In dynamic quenching, charge transfer occurs and the fluorescence is quenched when the electron acceptor collides with the excited fluoro-
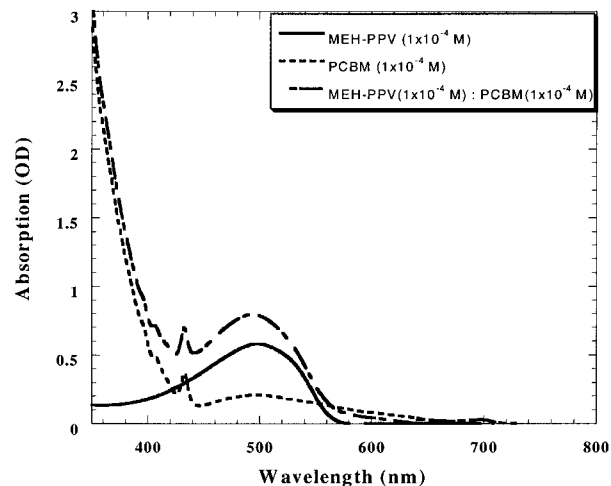

Figure 2 Absorption spectra of (a) MEH-PPV (1 × 10^{-4}M), (b) PCBM (1 × 10^{-4}M), and (c) MEH-PPV (1 × 10^{-4}M) plus PCBM (1 × 10^{-4}M).

phore. Because the collision between the quencher and the fluorophore affects only the excited state of the fluorophore, no changes in the absorption spectrum are expected. On the contrary, the formation of ground-state complex in static quenching will perturb the absorption spectra of the fluorophore. Thus, by careful examination of the absorption spectrum, one can attempt to distinguish static and dynamic quenching.

The absorption spectra of MEH-PPV in solution, of PCBM in solution, and MEH-PPV–PCBM in solution (all in 1,2-dichlorobenzene) are shown in Figure 2. In the spectrum of pure MEH-PPV, there is a major broad peak centered at 500 nm. In the spectrum of pure PCBM, there is strong absorption in the UV at wavelengths <400 nm, whereas the absorption in the visible is relatively weak (at 500 nm the PCBM absorption is weak compared with that from MEH-PPV at the same concentration). No indication of a spectral shift is observed as the PCBM is added. For the mixture of MEH-PPV and PCBM, at the concentration of 1 × 10^{-4}M, (where the ratio of MEH-PPV monomers to PCBM is 1 : 1), the absorption spectrum is simply a superposition of the MEH-PPV and PCBM absorption spectra. Figure 2 clearly shows the absorption spectrum of the mixture is a linear combination of the spectra of each component, implying dynamic quenching. The data are consistent with the results of Zheng et al.[12]: even at the very high concentration of 2.3 × 10^{-4}M (where the concentration of MEH-PPV in their experiment is 1.3 × 10^{-5}M, resulting in a ratio of
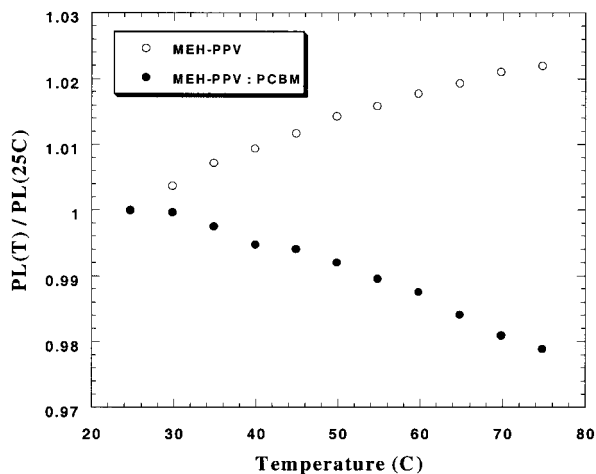
Figure 3 The photoluminescence relative to that at room temperature from MEH-PPV with concentration of $1 \times 10^{-4}M$ (open circles) and MBL-PPV–PCBM with concentrations of 1×10^{-4} and $1 \times 10^{-4}M$, respectively (solid circles) versus the temperature.

MEH-PPV repeat units to C_{60} to be $\sim 1:20$), they found neither a spectral shift nor any new absorption band due to the complex formation.

Zheng et al.[12] suggested, however, that a photoinduced charge transfer complex could be formed in the excited state rather than in the ground state. In this context, both quenching modes can be considered to arise from complex formation, the major difference being the lifetime of the complex. In dynamic quenching, the complex is transient and charge transfer is diffusion limited, whereas in static quenching, the fluorophore and the quencher are bound for a period much longer than the lifetime of the excited state.

Measurements of the temperature dependence of K_{SV} support the interpretation in terms of dynamic quenching. For dynamic quenching at high temperature, the larger thermal energy will facilitate the diffusion of the quencher towards the fluorophore. Thus, K_{SV} is expected to increase with temperature. In contrast, for static quenching, high temperature will decrease the stability of the complex and thereby reduce K_{SV}.

The temperature dependence of the PL obtained from MEH-PPV and MEH-PPV–PCBM solutions are illustrated in Figure 3. To show the change of PL more clearly, the PL data are normalized to the value at room temperature. The fluorescence from the pure polymer increases slightly with increasing temperature; the absolute value is 2% larger at 75°C than at room temperature. This increase could result from a change in conformation, with the polymer chain possibly more extended at high temperature. After addition of PCBM, the absolute PL value is reduced by 17% through quenching ($PL^0/PL \approx 1.2$), and the PL decreases with temperature as shown in Figure 3. In the MBL-PPV–MV^{2+} system, the temperature profile is opposite to that of MEH-PPV–PCBM.[11] The quenched fluorescence of MBL-PPV is "unquenched" at high temperature because the thermal energy dissociates the MV^{2+} acceptor from the MBL-PPV chain. The temperature profile shown in Figure 3 provides direct evidence that the basic quenching mechanism in MEH-PPV–PCBM is dynamic.

The K_{SV} value, $2 \times 10^3 M^{-1}$, obtained for MEH-PPV and PCBM dissolved in 1,2-dichlorobenzene, is large compared with that obtained for small molecule fluorophores but small compared with that obtained for MBL-PPV and MV^{2+} in aqueous solution. The enhanced fluorescence quenching observed for the MBL-PPV to MV^{2+} system (with LiSO$_3$ terminal groups on the side-chains of the PPV derivative) arises from a combination of two effects. First, one concludes from the concentrations used in the experiments that a single MV^{2+} acceptor quenches the fluorescence emission from an entire macromolecule.[9] Second, in aqueous solution, there is an equilibrium,

$$-SO_3^-Li^+ \Leftrightarrow -SO_3^- + Li^+ \qquad (5)$$
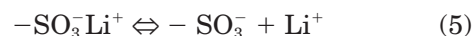
such that the luminescent polymer is negatively charged (anionic). As a result, the positively charged acceptor and the anionic polymer form a weakly bound complex, thereby significantly enhancing the local concentration of quencher molecules in the proximity of the luminescent polymer. Because the latter effect is absent in the MEH-PPV–PCBM system, we expect K_{SV} to be much smaller than in the MBL-PPV–MV^{2+} system. Comparison of the two indicates that complex formation (bound by the Coulomb attraction) leads to an enhancement in K_{SV} by a factor of $\sim 10^4$. Moreover, when the Coulomb attraction is enhanced by adding more charges to the quencher, K_{SV} increases.[16] On the other hand, comparison with *trans*-stilbene–MV^{2+}, where $K_{SV} \approx 15$ and where both components are diffusively mobile, indicates that a single acceptor in contact with an MEH-PPV macromolecule can indeed quench the luminescence from hundreds of repeat units.

CONCLUSIONS

Fluorescence quenching studies of MEH-PPV by PCBM in solution yield a value for the Stern–Volmer (quenching) constant of $2 \times 10^3 M^{-1}$. The absorption spectra of MEH-PPV in solution, PCBM in solution, and MEH-PPV–PCBM in solution show neither a spectral shift nor a new band, implying a dynamic quenching mechanism. Measurements of the temperature profiles of MEH-PPV in solution and MEH-PPV–PCBM in solution indicate that the basic quenching mechanism is dynamic rather than static.

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