The photophysical properties of chromophores at high (100 mM and above) concentrations in polymers and as neat solids[†]

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The absorption, fluorescence, and photostability of five conjugated chromophores: perylene, 2,5,8,11-tetra-*t*-butyl perylene (TTBP), perylene orange (PO), perylene red (PR), and a zwitterionic Meisenheimer complex (MHC), are studied as a function of concentration in poly(methyl methacrylate) (PMMA). At 1 mM concentrations, all five molecules exhibit properties consistent with unaggregated chromophores. At higher concentrations, perylene and PO both exhibit excimer formation, while TTBP, PR, and the MHC retain their monomeric fluorescent lineshapes. In these three molecules, however, the fluorescence decay times decrease by 10% (TTBP) to 50% (MHC) at concentrations of 100 mM in PMMA. The fluorescence properties of these highly concentrated samples are sensitive to the sample preparation conditions. In the neat solid where the effective concentration is on the order of 1 M, all three molecules exhibit very fast fluorescence decays, on the order of 150 ps or less, despite the fact that they retain their basic monomeric fluorescence lineshape. In addition to the enhanced nonradiative decay at high concentrations, these three molecules also undergo a concentration-dependent photobleaching. The combined effects of intermolecular nonradiative decay channels and photobleaching appear to be a general obstacle to achieving highly concentrated dye-doped solids.

Introduction

Electronic energy transfer (EET) between identical chromophores plays an important role in a variety of technological applications of organic electronic materials. In organic solar cells, photocurrent generation relies on exciton diffusion to charge separation regions where the photoexcitations are ionized into electron-hole pairs.¹⁻³ Conjugated polymer fluorescence sensors rely on energy transport along the polymer backbone, which allows a single binding event to modulate the fluorescence output of multiple chromophore units.⁴⁻⁶ The mobility of excitations is what gives rise to the superquenching or amplification effect in such sensor systems. In both applications, one wants to optimize the EET properties of a given material. In organic light-emitting diodes, on the other hand, exciton diffusion can lead to luminescence quenching at defect sites which is detrimental to device performance.⁷ In all three applications, optimizing device performance depends on understanding the underlying chemical mechanism of the EET. The basic physics of EET is well-studied, especially in the limit of the incoherent dipole-dipole interaction, or Forster resonance energy transfer (FRET). In this limit, Forster and later investigators⁸⁻¹³ have shown how FRET occurring between identical chromophores in a concentrated sample leads to an effective diffusion constant for the excitation,

$$D = A \rho^{4/3} R_0^6 \frac{1}{\tau_{\rm rad}}$$
(1)

where ρ is the chromophore number density, R_0 is the Forster radius for donor–donor FRET, τ_{rad} is the radiative lifetime of the isolated donor, and A is a constant on the order of 0.5.¹⁴ Given the diffusion constant D, the 3-D diffusion length of the exciton L_D is given by

$$L_{\rm D} = \sqrt{6D\tau_{\rm fl}} \tag{2}$$

where $\tau_{\rm ff}$ is the fluorescence lifetime of the donor. These two equations provide a straightforward way to predict energy transport properties in organic materials, assuming that energetic disorder, which can lead to anomalous diffusion,¹⁵⁻¹⁸ does not play a significant role. A quick calculation demonstrates that, given a Forster radius $R_0 = 5$ nm (an upper limit for most commonly used organic dyes), in order to achieve a diffusion length of 1 nm or more requires dye molecule densities on the order of 10^{18} molecules cm⁻³ or greater, or > 1 mM (milli-molar). Such high densities are typically found in conjugated organic solids and in self-assembled chromophore aggregates, but in both cases the spectroscopy can be complicated by the presence of intermolecular electronic species like delocalized exciton and excimer states.19-21 The presence of chemical impurities, like carbonyl groups, in conjugated polymer samples can also complicate the interpretation of experimental results.^{22,23} It is also difficult to vary ρ continuously in such systems due to phase separation. Ideally, one would be able to tune ρ by varying the solid-state concentration of a monomeric chromophore, which is resistant to aggregation and self-quenching. Such a system would

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[†] The HTML version of this article has been enhanced with additional colour images.



Fig. 1 Structures of perylene, perylene red, Meisenheimer complex, tetra-*tert*-butylperylene, and perylene orange.

not only provide a way to test the validity of diffusive theories of Forster energy transport, but would also find applications in solid state dye lasers and organic light emitting diodes.

In principle, it should be possible to control chromophore-chromophore interactions by modifying the chemical structure of the dye, e.g. by adding bulky sidegroups, which insulate the conjugated portion of the molecule. There are several studies, which examine the role of such steric modifications.^{24–27} While valuable, these studies often include only a partial characterization of the photophysical properties. For example, the steady-state fluorescence lineshape of the monomer in dilute solution is compared with that of a highly concentrated sample, without examining other possible effects, like self-quenching and photostability. In this paper, we present a more complete study of the concentration-dependent photophysical properties of a series of visible-absorbing chromophores in poly(methyl methacrylate) (PMMA). The molecules are shown in Fig. 1. In addition to perylene, we examine three sterically hindered perylene derivatives: 2,5,8,11-tetratert-butyl perylene (TTBP), perylene orange (PO), and perylene red (PR). The perylenes have well-studied spectroscopic properties and are commonly used in devices like lasers²⁸ and organic light-emitting diodes.²⁹ We also study a zwitterionic spiro-cyclical complex, denoted as the Meisenheimer complex (MHC)³⁰ whose nonplanar geometry should inhibit the cofacial aggregation commonly seen in polycyclical aromatic hydrocarbons. We compare the photophysical properties of this set of molecules for dilute solutions, concentrated solutions, and in the solid state. In particular, we are interested in how the monomer emission changes at high chromophore concentrations, whether due to the formation of new emitting states, like excimers, or due to enhanced nonradiative quenching. We also compare the photostability of the concentrated monomer systems with that of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), a widely studied conjugated polymer. We find that although some of the sterically hindered pervlenes retain their monomeric emission spectra and lifetimes up to very high ($\sim 100 \text{ mM}$) concentrations, such high concentrations also lead to accelerated photobleaching. For the molecules studied here, chromophore-chromophore interactions lead to chemical reactions which can be either reversible (excimer formation) or irreversible (photobleaching), but in either case they prevent the realization of dye/polymer solids with chromophore concentrations comparable to those of conjugated polymer films.

Experimental

Perylene orange (PO) and perylene red (PR) were received from BASF. PR was purified by column chromatography (silica gel, and dichloromethane as eluting solvent). All other materials including perylene, were purchased from Aldrich and used without further purification. Ultrapure water from a MilliQ filtration was used throughout the experiments.

The zwitterionic Meisenheimer complex, N', N'', N'''-tri(isopropyl)-4-oxo-6-(isopropylimino)-2-s-(2*H*)triazinespiro-1'-2',4',6'-trinitrocyclohexadienylide (MHC) was synthesized and purified according to a previously reported method.³⁰ An overall yield of 15.5% for the red MHC crystals was obtained. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.22$ (d, J = 6.9 Hz, 6 H), 1.33 (d, J = 7.2Hz, 6 H), 1.45 (d, J = 6.3 Hz, 6 H), 1.72 (d, J = 6.6 Hz, 6 H), 3.14 (septet, J = 6.9 Hz, 1 H), 3.87 (septet, J = 7.2 Hz, 1 H) 3.95–4.10 (m, 1 H), 4.18 (septet, J = 6.6 Hz, 1 H), 4.30 (d, J =9.0 Hz, 1 H), 9.01 (s, 2 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 19.90, 22.01, 23.11, 24.10, 51.05, 51.10, 53.12, 58.40, 82.28, 120.13, 125.54, 130.83, 145.01, 154.71 ppm. Elemental analysis for MHC (C₂₀H₃₁N₇O₇) calculated: C, 49.91%; H, 6.44%; N, 20.38%; found; C, 49.86%; H, 6.51%, N, 20.09.

Synthesis of 2,5,8,11-tetra-tert-butylperylene (TTBP)

Our synthesis of TTBP involves some variations from the procedure usually cited in the literature, ^{31,32} and so we report it in detail here. In a 100 mL round bottom flask perylene (0.50 g, 0.002 moles) was added to 2-methyl-2-chloropropane (50 mL) previously dried over activated molecular sieves. The mixture was sonicated and agitated to brake up the large pieces of perylene and form a finely dispersed suspension. Aluminum trichloride anhydrous powder (1.0 g, 0.0075 moles) was gradually added to the rapidly stirring mixture of perylene in 2-methyl-2-chloropropane. The mixture was then refluxed under argon for 12 h. An additional 25 mL of 2-methyl-2-chloropropane was added followed by aluminum trichloride (1.0 g, 0.0075 moles), and refluxed for 12 h more. Finally another 20 mL of 2-methyl-2-chloropropane was added along with aluminum trichloride (1.0 g, 0.0075 moles) and refluxed

under argon for 12 h until a TLC (silica gel, solvent; 2:1 hexane: dichloromethane) of the reaction mixture gave only one product spot. The organic phase was then agitated with 100 mL portions of distilled water until the aqueous phase became clear. The dark viscous organic mixture was spread on a flat glass dish and heated at 170 °C over a hot plate in a well ventilated area. The organic mixture was allowed to bake for 24 h or until smoke ceased to evolve. The black tar residue $(\sim 0.9 \text{ g})$ was dissolved in dichloromethane (5 mL) followed by hexanes (10 mL). Purification of the crude product was achieved through column chromatography (activated neutral alumina, and hexanes as the eluting solvents). A black residue was retained at the top of the column while the yellow product was slowly eluted through and collected. The solvent was removed under reduced pressure and a yellow powder was obtained with a yield of 0.45 g (49%). The ¹H NMR (400 MHZ, CDCl₃) of the product is consistent with the reported values, $\delta = 1.50$ (s, 36 H), 7.64 (s, 4 H), 8.25 (s, 4 H). A low resolution mass spectrum of the purified compound yielded a single, large molecular ion peak at the expected MW = 476. Higher MW peaks are only a few percent or less of the parent ion peak, with none where they would be expected for >4 tertbutyl groups, indicating that higher molecular weight products of the substitution reaction are negligible.

Preparation of the polymer films

Poly(methyl methacrylate) (PMMA, 1.0 g, 120 000 average molecular weight) was dissolved in tetrahydrofuran (THF, 10 mL) to make a concentration $C_{\rm PMMA} = 0.10$ g PMMA mL⁻¹ of THF. A solution of perylene, PO, PR, MHC or TTBP in THF ($C_{\rm dye} = 0.02$ molar) was prepared and stored in the dark. Note $C_{\rm dye}$ and $C_{\rm PMMA}$ have different units. Different ratios of PMMA in THF solution were combined with the pre-prepared solutions of the dyes in THF to make a concentration $C_{\rm doped}$ in the polymer using the formula:

$$C_{\text{doped}} = \frac{\text{moles dye}}{\text{volume PMMA}} = \frac{C_{\text{dye}} \times V_{\text{dye solution}}}{C_{\text{PMMA}} \times V_{\text{PPMA solution}}/d} \quad (3a)$$

which can be rearranged to obtain

$$\frac{V_{\text{PMMA solution}}}{V_{\text{dye solution}}} = \frac{C_{\text{dye}} \times d}{C_{\text{PMMA}} \times C_{\text{doped}}}$$
(3b)

where V is either the volume of dye solution or PMMA solution in mL and d = 1.19 g cm⁻³ is the density of the polymer. Glass microscope slides (cut to 2.5×2 cm) were washed with acetone, wiped clean and placed on a spin coater (Laurell, WS-400B-6TFM-LITE). While the glass slide was spinning at 3600 rpm, 0.1 mL of the dye/PMMA mixture in THF was added using a pipette. The sample was allowed to spin for 1 min, then immediately loaded into a Janis ST-100 continuous-flow cryostat and placed under vacuum (less than 10^{-4} Torr) to prevent photooxidative damage. The solid samples were prepared by spin-casting the dye/THF solution directly onto the microscope slide. The liquid samples were prepared by diluting the dye/THF solution until their optical densities in a 1 cm length cuvette were less than 0.1 at and above the excitation wavelength.

Thermal annealing of the TTBP/PMMA films

A 0.3 M TTBP in PMMA was prepared as described previously. The sample was introduced in a sealed glass container and purged with argon. Then it was heated in an oil bath set at 130 °C (Tg of PMMA ~ 110 °C) for no more than 20 min. To insure the integrity of the TTBP in PMMA, an absorption spectrum of the TTBP/PMMA polymer sample was collected before and after the annealing process which showed no measurable decrease in absorption or change in spectral shape. Heating for longer than 20 min resulted in a decrease in absorption, and such samples were not used for the spectroscopic measurements.

Absorption, fluorescence spectra and photophysics

Ground state absorption spectra of the polymer films were collected using an Ocean Optics SD2000 absorption spectrometer. Steady state fluorescence was determined using Spex Fluorolog Tau-3 fluorescence spectrophotometer with front face excitation ($\lambda_{ex} = 400$ nm) of the samples. Fluorescence lifetimes were measured by exciting the samples using pulses centered at 400 nm, derived from the frequency doubled output of a 40 kHz regeneratively amplified Ti:Sapphire laser system with a pulse width of 150 fs. To purify the polarization of the excitation beam, the laser was passed through a calcite polarizer before exciting the sample. The fluorescence emission of liquid samples was collected at 90° relative to the excitation, whereas for polymer and solid film samples the incident angle of the exciting laser beam was about 10° relative to the film surface normal. The excitation pulses exhibited linear polarization, and the angle between the polarization of the collected fluorescence light and that of the excitation light was adjustable for anisotropy measurements, using a polarizer that was placed in the emission beam path. The emitted light was collimated and focused into a monochromator (Spectra Pro-150 spectrometer) attached to a picosecond streak camera (Hamamatsu C4334 Streakscope), which provides both time and wavelength-resolved fluorescence data, with a spectral resolution of 2.5 nm and a temporal resolution of 15 ps.

Photobleaching studies

The photobleaching studies were done in a manner similar to that used previously to evaluate conjugated polymers.³³ All samples were maintained under an active vacuum of 10^{-4} Torr in a cryostat. The samples were irradiated with the 400 nm femtosecond laser pulses, with an average power of 10 µW focused to an 80 µm diameter spot. Since PR samples have low absorbance at 400 nm, the photobleaching was also studied using 532 nm cw excitation. Data from both types of experiments were consistent. Increasing or decreasing the laser pulse energy by a factor of 3 did not change the observed photobleaching rates; in other words, the photobleaching depended only on the number of absorbed photons, as calculated from eqn (5), and not on the peak power of the pulse. Thus effects due to multiphoton absorption from the excited state appear to be negligible given the powers used here.

The photon flux Φ , which is the number of photons hitting a unit area of the sample per second, is given by

$$\Phi = \frac{I_{\text{laser}}}{E_{\text{photon}}} = \frac{P/\pi r^2}{hc/\lambda} \tag{4}$$

where $E_{\text{photon}} = \frac{hc}{\lambda}$ is the energy of the laser photons, λ is the laser wavelength, and *P* is the measured laser power. The radius *r* of the focused laser beam at its focus is obtained by translating a knife-edge across the focal point. The rate *R* at which each molecule absorbs the photons is

$$R = \Phi \sigma \tag{5}$$

where σ is the absorption cross section of the dye molecule at the laser wavelength, obtained from the absorption coefficient.³⁴ The highest value of *R* in our measurements was a few MHz. Since the fluorescence lifetimes are less than 10 ns, it is unlikely that the molecule has a chance to see another photon while it is in its electronically excited state. The average number of photons a molecule will have absorbed after a time *t* would be *Rt*. The fluorescence signal is proportional to the number of molecules in the region illuminated by the laser beam. The ratio of the fluorescence signal relative to its initial value gives the probability that the dye molecule has photobleached after absorbing *Rt* photons.

Results and discussion

Fig. 2 shows the absorption and emission spectra of the five molecules in both dilute (1 mM) and concentrated (100 mM) PMMA films. Both perylene and PO show clear signatures of the broad, redshifted excimer emission at higher concentrations. Excimer formation has been observed previously for both molecules in concentrated PMMA solids.^{35,36} The lifetimes of the excimer emissions are generally longer than those of the monomer singlet states, but their fluorescence quantum yields are generally lower, and thus excimer formation is usually regarded as detrimental to luminescence efficiency.³⁷

It should be noted that even though the excimer emission contribution comprises 96% of the steady state emission in PO (Table 1), this does not necessarily mean that 96% of the PO molecules are bound in excimers. Rapid EET from monomers to the low-lying excimer states, which act as luminescence traps, can lead to the observed enhancement even at relatively low excimer populations.³⁶ In contrast to the end-substituted perylenes, ring-substituted perylenes like TTBP and PR showed no identifiable excimer component at the highest concentrations, as can be seen from Fig. 2c and d. In fact, even solid films of these two molecules, cast from a THF solutions onto a glass surface, retained their monomeric fluorescence lineshape. This type of monomer emission is also seen in concentrated solutions and solid films of the nonplanar MHC, which is shown in Fig. 2e.

A fluorescence spectrum similar to that of the monomer does not by itself prove the absence of intermolecular interactions. Such interactions can also manifest themselves as nonradiative decay channels, which can be investigated using time-resolved fluorescence measurements. Fig. 3 and Table 1 summarize the fluorescence lifetime data for the non-excimerforming molecules. In Fig. 3a, the fluorescence decay of different concentrations of TTBP in PMMA is shown. The lifetime of the 1 mM concentration, 4.4 ns, is similar to that measured previously in other polymers and in dilute solution.^{38,39} At 100 mM concentration, the lifetime of 4.1 ns is only slightly shorter. For concentrations greater than 100 mM, the lifetime rapidly decreases and becomes multi-exponential. Similar behavior at these concentrations was observed for TTBP in other polymers, including polystyrene and Zeonex. This suggests that the concentration-dependent quenching is not sensitive to the details of the structure of the polymer host, but is primarily a function of the proximity of the dopant chromophores to each other. The multiexponential nature of the decay probably reflects the presence of several different types of aggregate quenching conformations. It is worth noting that the spectroscopic properties of the TTBP/PMMA



Fig. 2 Fluorescence (solid) and absorption (dashed) spectra of different chromophores in PMMA at different concentrations. (a) Perylene, 1 mM and 100 mM from left to right, respectively. (b) PO, 1 mM and 100 mM from left to right, respectively. (c) TTBP, 1 mM, 100 mM and fluorescence of the solid film from left to right, respectively. (d) PR, 1 mM, 100 mM and fluorescence of the solid film from left to right, respectively. (e) MHC, 1 mM, 100 mM and fluorescence of the solid film from left to right, respectively. (e) MHC,

Table 1 All fluorescence decays are measured using 400 nm excitation. The normalized biexponential decays are parameterized by the time constants τ_1 and τ_2 (in nanoseconds) with pre-exponential factors A₁ and A₂, respectively. The % excimer is calculated from the relative areas of the monomer and excimer lineshapes in the steady-state fluorescence spectra

Name of compound	Excimer formation at 100 mM?	% excimer	1 mM $ au_{ m ns}$	100 mM				Solid			
				A_1	$ au_1$	A_2	τ_2	A_1	$ au_1$	A_2	τ_2
Perylene	Yes	85%									
Perylene orange	Yes	96%									
TTBP	No		4.4	1	4.1			0.62	0.06	0.38	0.53
Perylene red	No		5.6	1	4.8			0.64	0.08	0.36	0.41
Meisenheimer	No		7.1	0.6	2.5	0.4	6.8	0.72	0.15	0.28	0.87
Dimethyl-POPOP	No	—	1.3	0.64	0.8	0.36	2.67				



Fig. 3 Natural log of normalized decay of different chromophore. (a) TTBP: 1 mM in PMMA upper line, 100 mM in PMMA middle line and 200 mM in PMMA bottom line. (b) PR: 1 mM in PMMA upper line, 100 mM in PMMA bottom line. (c) MHC: 1 mM in PMMA upper line, 100 mM in PMMA bottom line.

films can depend on preparation conditions at chromophore concentrations of 100 mM and higher. Fig. 4 shows the fluorescence decays for 1 mM TTBP in PMMA along with 300 mM TTBP in PMMA under two different preparation conditions. In the first preparation, the polymer solution was spin cast onto a glass substrate at 500 rpm for 1 min. The fluorescence decay of this sample showed a biexponential behavior in which 63% of the signal decayed with time $\tau_1 =$ 0.45 ns and 37% decayed with a time $\tau_2 = 2.08$ ns. If the same sample is then briefly heated to 130 °C and then cooled in air, the fluorescence lifetime is dramatically lengthened to another



Fig. 4 Normalized natural log of fluorescence decay of TTBP in PMMA. (a): 1 mM; (b): 300 mM in PMMA annealed; (c): 300 mM in PMMA un-annealed. Inset: steady state fluorescence of 300 mM TTBP in PMMA, before and after annealing.

biexponential decay where 73% of the fluorescence decays with $\tau_1 = 2.37$ ns and 27% decays with a $\tau_2 = 4.96$ ns, close to that of the dilute sample. The steady state fluorescence spectrum, shown in the figure inset, remains the same during this process. We attribute the longer fluorescence lifetime after thermal annealing to the disruption of molecular aggregates in the polymer. A less pronounced effect on the 100 mM films is observed for different spin-coating speeds. By spinning the sample at 3600 rpm instead of 500 rpm, the emission spectrum sharpens slightly, although this sharpening is not accompanied by any change in the fluorescence lifetime. This sensitivity to preparation conditions may explain why the observed fluorescence spectrum for the solid TTBP obtained from solution deposition is slightly different from that obtained by vacuum evaporation.⁴⁰

Similar trends in the fluorescence lifetime are obtained for the other two molecules which retain their monomeric emission at high concentrations. PR also shows little change between 1 and 100 mM concentrations in PMMA, as can be seen from Fig. 3b. The measured lifetime of the 100 mM sample is 4.8 ns, a 15% drop from the 5.6 ns lifetime of the 1 mM sample. The MHC shows a more dramatic decrease in lifetime with concentration. At 100 mM, the decay becomes biexponential, with one component at 6.8 ns being close to that of the single decay time observed for the 1 mM samples (7.1 ns). The other component, at 2.5 ns, is much more rapid and composes 60% of the total decay. Thus both PR and the MHC exhibit more self-quenching at 100 mM than TTBP, although PR is still relatively long-lived. In the neat solids, where the effective chromophore concentration is on the order of 1 M, all three molecules undergo much more rapid quenching, as can be seen from Table 1. For all three, the fluorescence decay is multiexponential, with at least 60% of the decay occurring within 150 ps or less. While there is still no sign of



Fig. 5 Anisotropy decay of TTBP in PMMA, (a): 1 mM TTBP in PMMA; (b): 100 mM TTBP in PMMA.

new species in the emission, there are clearly strong interactions in the neat solid which effectively deactivate the singlet excited state and quench the fluorescence.

Even at 100 mM, the TTBP/PMMA films demonstrate phenomena which are reminiscent of conjugated polymer films. Evidence for rapid interchromophore EET is obtained from the anisotropy decays shown in Fig. 5. We calculated the Forster radius $R_0 = 3.9$ nm for TTBP,³⁹ and at a concentration of 1 mM, the average interchromophore distance is 10 nm, leading to negligible EET during the excited state lifetime. At 100 mM, however, the average interchromophore separation has decreased to about 2 nm, and intermolecular EET leads to a rapid randomization of the transition dipole moment orientation and thus a rapid fluorescence depolarization. The decay of the fluorescence polarization can be predicted by a statistical mechanical approach which takes into account the random distribution of chromophore separations.⁴¹⁻⁴³

$$r(t) = \frac{S_{||}(t) - S_{\perp}(t)}{S_{||}(t) + 2S_{\perp}(t)} = \exp\left[-\sqrt{t/\tau}\right]$$
(6)

$$\tau = \frac{9\lambda\tau_{\rm fl}}{16\pi^2 R_0^6 \rho^2 \gamma^2 \Gamma(1/2)^2}$$
(7)

Where *r* is the anisotropy and $S_{\parallel}(t)$ and $S_{\perp}(t)$ are the fluorescence signal parallel and perpendicular to the excitation polarization, respectively. $\Gamma(x)$ is the gamma function, γ is a factor that takes orientational disorder into account, and $\lambda = 2$ for donor-donor transfer. R_0 , $\tau_{\rm fl}$, and ρ are as defined in eqns



Fig. 6 Photobleaching of the fluorescence of selected dyes in solid state samples. (a): 1 mM TTPB in PMMA; (b): neat MEHPPV film; (c): 30 mM TTBP in PMMA; (d): 100 mM TTBP in PMMA.

(1) and (2). This theory predicts the anisotropy decay time $\tau =$ 16 ps, given a number density of 6×10^{19} molecules cm⁻³. which corresponds to 100 mM. The experimentally observed anisotropy decay time $\tau = 30$ ps is in reasonable agreement with this value. The deviation from the theoretical value may be the result of anomalous subdiffusion resulting from an inhomogeneous energetic distribution of chromophores in the solid.15-18 But if we neglect anomalous diffusion effects, the same theory allows us to estimate the diffusion constant and the diffusion length for the excitation. We find the diffusion constant $D = 7.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and the diffusion length $L_D = 14$ nm. This diffusion length is comparable to that obtained by several studies on conjugated polymers using variable concentrations of quenchers and measuring the fluorescence decay as a function of quencher concentration.44-46 In the conjugated polymers, the increased chromophore concentration $(10^{21} \text{ cm}^{-3} \text{ versus } 10^{20} \text{ cm}^{-3})$ is probably offset by a lower fluorescence lifetime (several hundred ps versus 4 ns), leading to the similar estimates for $L_{\rm D}$.

Although the concentrated dye/PMMA samples would appear to be fair mimics of amorphous conjugated polymers, all the samples in this study had an important practical drawback. We found that all of our concentrated ($\geq 100 \text{ mM}$) dye samples have much lower photostability than either dilute samples or conjugated polymer samples. By measuring the absorbance of the sample and the laser power, we can estimate the number of absorption events per chromophore per time, and plot the photobleaching as a function of molecular absorptions. Fig. 6 shows the evolution of the fluorescence intensity coming from TTBP/PMMA samples under constant laser exposure. The initial photobleaching rate of the 100 mM sample has a slope of 2.5×10^{-4} per molecular absorption and is observed to lose 60% of its fluorescence intensity within a few minutes. A 30 mM sample undergoes a slower decline, and a 1 mM sample has no observable change over the same period of time. The average lifetime of a TTBP molecule in a 100 mM PMMA film is only about 10^4 absorptions, which is 10^2-10^4 times less than isolated perylene chromophores.⁴⁷ PR also exhibits a concentration-dependent photobleaching, but the 100 mM sample is longer-lived, with an initial slope of 4.1 \times 10^{-7} per molecular absorption and an effective lifetime of about 10⁶ absorption cycles. The photobleaching kinetics of concentrated MHC films were similar to those of the perylenes, with an intermediate photostability. Neat MEH-PPV undergoes a slight decay after 10⁸ absorption events, but is markedly more stable than either the TTBP or PR films. The rate of TTBP photobleaching does not depend on the chemical structure of the host polymer, since similar photobleaching kinetics are observed for TTBP in polystyrene and Zeonex. The detailed kinetics of the photobleaching are quite complicated, since the concentrations and thus the photobleaching rate change with time. But since the initial rate does not depend on the host polymer, it is likely that irreversible chromophore-chromophore reactions are responsible. Examination of the absorption spectrum of a photobleached PR sample showed that the decrease in visible absorption was accompanied by an increase in a broad, featureless absorption in the UV region below 300 nm, suggesting that the photoproducts have lost conjugation. Related mechanisms have been proposed for the concentration-dependent photobleaching of xanthene dyes in inert matrices.⁴⁸

Conclusion

In this work we have explored the photophysical properties of highly concentrated polymer solutions of sterically hindered conjugated chromophores. We found that both ring substituted pervlenes and a nonplanar spiro compound can retain their monomeric emission properties even in the neat solid, where the chromophore concentration is ~ 1 M. Fluorescence self-quenching, however, places an upper limit on their concentration in an amorphous polymer of ~ 0.1 M, however, if high (>80%) fluorescence quantum yields are desired. Even at these lower concentrations, rapid photobleaching limits the practical usefulness of such highly concentrated dye-doped solids. The strategy of preventing aggregation by steric hindrance is thus only partially successful in these compounds. It appears that a better understanding of the mechanisms of photobleaching and nonradiative quenching in dense chromophore systems is necessary in order to eventually achieve stable, highly luminescent dye/polymer systems with dye concentrations comparable to the chromophore densities in conjugated polymer systems.

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