Mater. Res. Soc. Symp. Proc. Vol. 1392 © 2012 Materials Research Society
DOI: 10.1557/opl.2012.774

Photophysical Properties of a Nonlinear Dye in PMMA at High Concentration

Joy E. Haley[1], Jonathan L. Flikkema[1,2], Weijie Su[1,3], Douglas M. Krein[1,3], and Thomas M. Cooper[1]

[1]Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, OH 45433
[2]SOCHE Student Research Program, Dayton, OH 45420
[3]General Dynamics Information Technology, Dayton, OH 45431

ABSTRACT

The effects of high concentration on the photophysical properties of a nonlinear material have been of interest for some time in our group. It is well known in the literature that for a nonlinear absorbing dye to be the most effective, high concentrations are needed. The problem is that most photophysical studies in solution are done at low concentration. These low concentration studies are important for understanding inherent materials properties but it is also important to understand what happens in a material at high concentration. In addition to this, efforts have been made to study the effects of incorporating a dye into a solid matrix environment to better understand the constraints this environment has to a given material. Preliminary results for a PMMA system reveal the formation of excimers (excited state dimers) with an increase in concentration. Excimers are forming from the triplet excited state of the E1-BTF. A rate constant for this formation is 2.3 x 10^6 M^{-1} s^{-1}. While rather slow, at high concentration the excimer is readily formed. This must be considered when making nonlinear absorption measurements since the excimer will certainly contribute to the overall nonlinearity.

INTRODUCTION

Development of two-photon absorbing materials has increased significantly recently due to their usefulness in various applications.[1] We are mainly interested in their use for nonlinear photonics.[2] These materials provide an advantage by exciting in the lower energy near-IR region, resulting in the inherent higher energy photons. Materials that possess good two-photon properties have been found to have either an asymmetrical D-π-A (donor-π-conjugated group-acceptor) or a symmetrical D-π-A-π-D or A–π-D-π-A structural motif leading to a large change in polarization upon excitation.[3] Recently we have focused our efforts on developing platinum containing two photon absorbing materials that possess both the asymmetrical and symmetrical structural motif. A large two photon cross section was observed in the chromophore with an A–π-D-π-A containing the benzothiazole ligand as the acceptor and the central platinum serves as the donor (E1-BTF).[4] It is well known in the literature that for a nonlinear absorbing dye to be the most effective, high concentrations are needed. Therefore the need arose to better understand the photophysical properties of this material at high concentration and also in a solid environment. Here we report initial findings on the chromophore E1-BTF in benzene and compare this to samples prepared by dissolving the dye into PMMA (poly methyl methacrylate). Shown in Figure 1 are a series of different concentration samples prepared ranging from 0.3 mM to 17 mM.

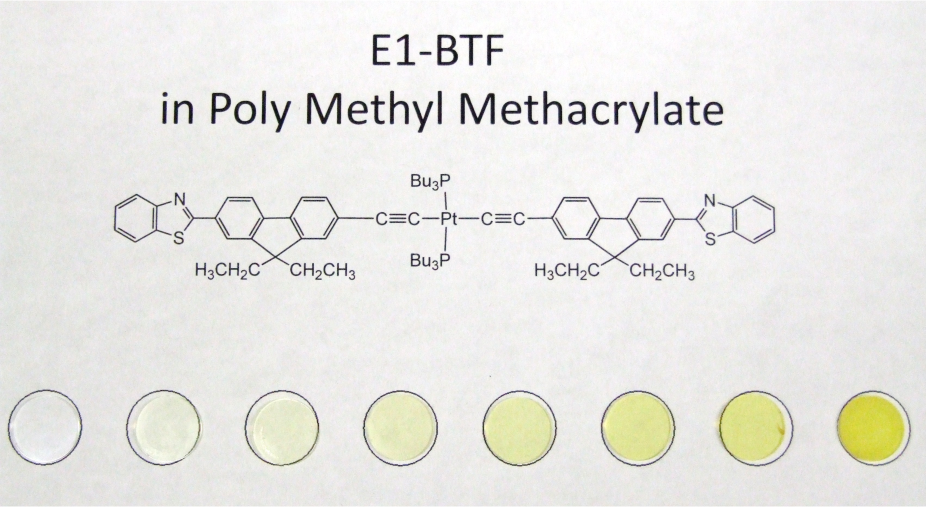

Figure 1. Structure of the chromophore E1-BTF including pictures of the PMMA samples prepared. From left to right are 0 mM, 0.3 mM, 0.5 mM, 1.1 mM, 2.2. mM, 4.4 mM, 8.8 mM, and 17.1 mM.

EXPERIMENTAL

E1-BTF shown in Figure 1 was synthesized according to previous methods.[4] Poly methyl methacrylate was purchased from Poly Sciences, Inc. with an intrinsic viscosity of 0.4 and a molecular weight of 25000. Samples were prepared by dissolving known quantities of dye with PMMA and the solvent was allowed to slowly evaporate. Samples were then cut into 1 mm discs and polished. For all of the solvents high optical quality was achieved except for the 17 mM sample. Here we observe haze in the sample due to phase separation of the PMMA and the dye upon evaporation of the solvent. Ground state UV/Vis absorption spectra were measured with a Cary 500 spectrophotometer. Steady state fluorescence measurements were done on a Varian Eclipse and emission time resolved measurements on a system from Edinburgh Instruments. Nanosecond transient absorption measurements were carried out using the third harmonic (355 nm) of a Q-switched Nd:YAG laser (Quantel Brilliant, pulse width ca. 5 ns). Pulse fluences of up to 8 mJ/cm^2 are typically used at the excitation wavelength. A detailed description of the laser flash photolysis has been previously described.[5]

RESULTS AND DISCUSSION

Shown in Figure 2 are the ground state absorbance data for the PMMA samples compared to E1-BTF in benzene. Absorbance data are given in Table 1. For the most part the spectral characteristics are quite similar for the lower concentration PMMA sample suggesting that the E1-BTF at lower concentration is similar as in solution. Unfortunately not much information is obtained on the samples at higher concentration. For the 17.1 mM sample we observe a long tail due to scatter. As mentioned previously this sample is not optically clear and most likely phase separation occurred following evaporation of the solvent putting a limit to the maximum concentration of around 10 mM. Aggregation of the E1-BTF in the sample at high concentration has not been addressed in this study. Any tailing observed in the ground state absorption spectrum certainly could be attributed to aggregation effects but at this point of study it is too difficult to separate this from any scattering effects.

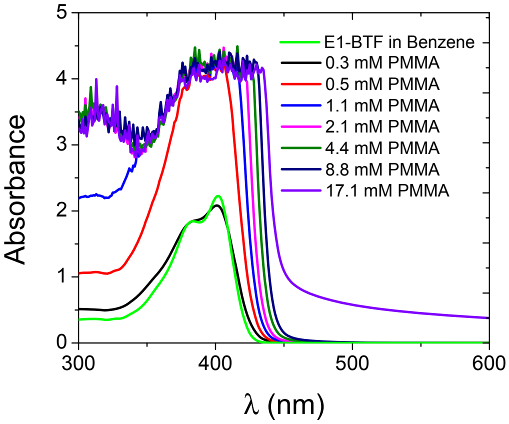

Figure 2. Ground state absorbance data of E1-BTF in PMMA compared to data in benzene. PMMA samples have a 1 mm path length.

Due to the heavy atom effect of the platinum intersystem crossing to the triplet excited state occurs readily. E1-BTF has moderately strong phosphorescence from the triplet excited state as shown in Figure 3a. The data has been normalized at the peak for comparison. Also shown is data measured in deoxygenated benzene. There is only a small change in the overall spectral appearance with variation in concentration. To better understand the kinetic properties of the dye we utilized time resolved emission exciting the samples at 375 nm with a pulsed

Table 1. Absorbance and Emission Properties of E1-BTF in PMMA

Sample	Abs Max	Ph Max	T_1-T_n Max ($t = 0$ μs)	T_1-T_n Max ($t = \sim 4$ ms)	τ_{T1}	τ_{T2}
0.3 mM	401 nm	567 nm	644 nm	533 nm	873 ± 74 μs	> 3 ms
0.5 mM	---	567 nm	639 nm	533 nm	1177 ± 181 μs	> 3 ms
1.1 mM	---	568 nm	645 nm	533 nm	977 ± 111 μs	>3 ms
2.1 mM	---	567 nm	644 nm	533 nm	737 ± 79 μs	> 3 ms
4.4 mM	---	567 nm	644 nm	533 nm	106 ± 22 μs	1500 ± 500 μs
8.8 mM	---	568 nm	649 nm	540 nm	47 ± 15 μs	764 ± 196 μs
17.1 mM	---	567 nm	640 nm	---	27 ± 7 μs	349 ± 48 μs
Benzene	402 nm	565 nm	660 nm	---	318 ns	---

xenon lamp. This data is shown in Figure 3b. For all of the PMMA samples we observe a growth and decay kinetic profile that is believed to be due to the formation of a triplet excimer (excited state dimer) and then decay of this species. Previous study of a similar system indicates excimer formation is highly probable with an increase in concentration.[6] To further evaluate the triplet excited state properties of the E1-BTF in PMMA nanosecond laser flash photolysis was

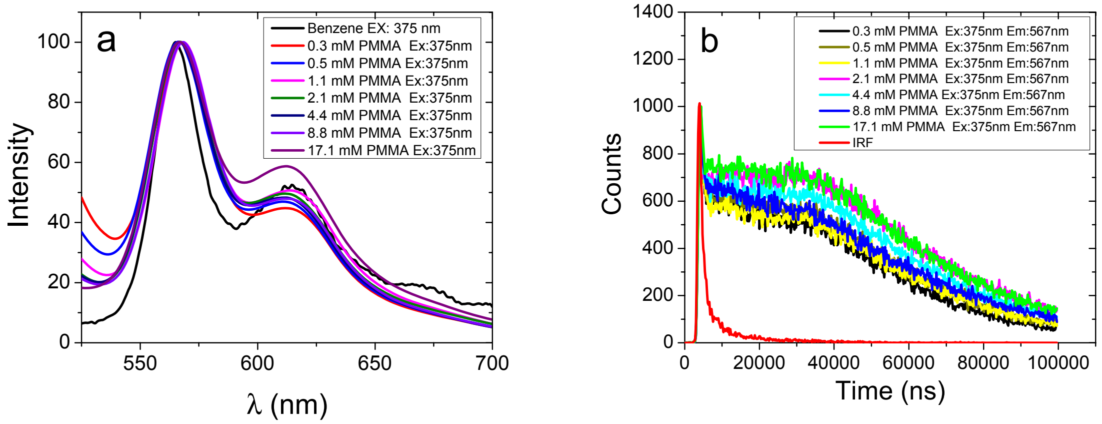

Figure 3. (a) Phosphorescence data of E1-BTF in PMMA at various concentrations. Data has been normalized at the peak. Samples were excited at 375 nm. Data taken in benzene under deoxygenated conditions. (b) Time correlated single photon counting data of E1-BTF in PMMA. All samples were excited at 375 nm with a front face geometry. Emission was monitored at 567 nm.

utilized. In this experiment the samples were excited at 355 nm (5 ns pulse) and probed with white light. Shown in Figure 4a are resulting normalized data immediately following the laser pulse. For the PMMA samples the spectral properties are similar but for E1-BTF in benzene there is a slight red shift. Also shown in Figure 4b are long time spectra for the samples (~ 4 ms after the pulse). It is interesting to note here that a large blue shift is observed

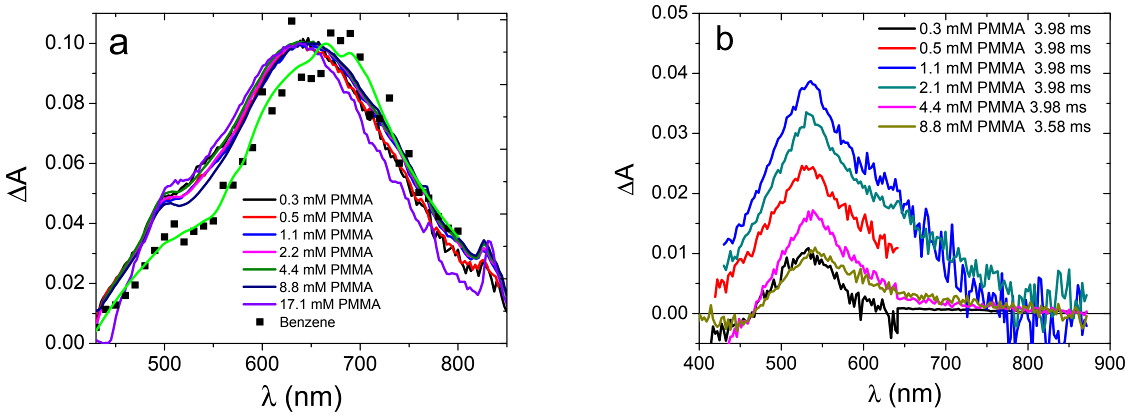

Figure 4. (a) Normalized nanosecond transient absorption data of E1-BTF in PMMA and benzene immediately following the laser pulse (time zero). All samples were excited at 355 nm. (b) Transient absorption data at long times (~ 4 ms) showing a blue shift in the peak.

from the time zero data indicative of formation of a new species. We believe this species to be the triplet excimer. It is not observed in benzene at low concentrations. At this time experiments have not been done to confirm if it is formed at high concentration in solution but we will pursue this in the near future. The peak maximum data are given in Table 1. The kinetic decays shown in Figure 5(a) show biexponential decay with a long lived species. The kinetic profiles were all fit to a biexponential decay and are given in Table 1. An increase in τ_1 is observed with an increase in concentration due to formation of the excimer. The data was fit to a pseudo first order quenching model ($k_{obs} = k_q + k_d[Q]$) as shown in Figure 5b and the rate constant for quenching is 2.3×10^6 M^{-1} s^{-1}. This is less than diffusion controlled and consistent with values previously determined for the platinum poly-yne PE2.[6] However the quenching does need to be considered when looking at the nonlinear absorption properties of the dye. Previously we determined that the excited state absorption plays a major role in the nonlinear absorption of a dye.[7] At high concentration the triplet excimer is readily formed and contributes to the overall nonlinearity of the E1-BTF. These results will be presented in a separate paper.

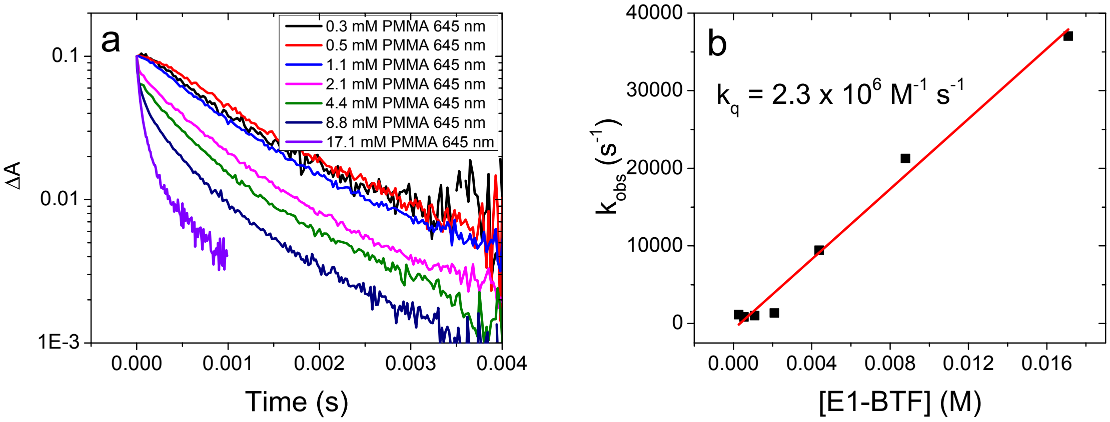

Figure 5. (a) Transient absorption kinetic decays at 645 nm for PMMA samples. Data has been normalized for comparison. Fits are given in Table 1. (b) Fit of k_{obs} versus E1-BTFconcentration to give the quenching constant for excimer formation of 2.3×10^6 M^{-1} s^{-1}.

CONCLUSIONS

Preliminary results for an E1-BTF/PMMA system reveal the formation of excimers (excited state dimers) with an increase in concentration. Excimers are forming from the triplet excited state of the E1-BTF as determined through time resolved phosphorescence data as well as time resolved transient absorption data. A rate constant for this formation is 2.3×10^6 M^{-1} s^{-1}. While rather slow, at high concentration the excimer is readily formed. This must be considered when making nonlinear absorption measurements since the excimer will certainly contribute to the overall nonlinearity.

ACKNOWLEDGMENTS

This work was supported by AFRL/RX contracts FA8650-09-2-5800 for J.L.F and F33615-03-D-5408 for D.M.K. and W.S.

REFERENCES

---

[1] He, G.S.; Tan, L.-S.; Zheng, Z.; Prasad, P.N. *Chem. Rev*. **108**, 1245 (2008)

[2] (a) Fleitz, P.A.; Sutherland, R.A.; Strogkendl, F.P.;Dalton, L.R.; *SPIE Proc*. **3472**, 91 (1998); (b) He, G.S.; Bhawalkar, J.D.; Zhao, C.F.; Prasad, P.N. *Appl. Phys. Lett*. **67**, 2433 (1995); (c) Ehrlich, J.E.; Wu, X.L.; Lee, L.Y.; Hu, Z.Y.; Roeckel, H.; Marder, S.R.; Perry, J. *Opt. Lett*. **22**, 1843 (1997)

[3] Marder, S.R.; Gorman, C.B.; Meyers, F.; Perry, J.; Bourhill, G.; Bredas, J.-L.; Pierce, B.M. *Science* **26**5, 632 (1994)

[4] Rogers, J.E.; Slagle, J.E.; Krein, D.M.; Burke, A.R.; Hall, B.C.; Fratini, A.; McLean, D.G.; Fleitz, P.A. Cooper, T.M.; Drobizhev, M.; Makarove, N.S.; Rebane, A.L.; Kim, K-Y,; Farley, R.; Schanze, K.S. *Inorg. Chem*. **46**, 6483 (2007)

[5] Rogers, J.E.; Cooper, T.M.; Fleitz, P.A.; Glass, D.J.; McLean, D.G. *J. Phys. Chem. A* **106**, 10108 (2002)

[6] Slagle, J.E.; Cooper, T.M.; Krein, D.M.; Rogers, J.E.; McLean, D.G.; Urbas, A.M. *Chem. Phys. Lett*. **447**, 65 (2007)

[7] Sutherland, R.L.; Brant, M.C.; Heinrichs, J.; Rogers, J.E.; Slagle, J.E.; McLean, D.G.; Fleitz, P.A. *J. Opt. Soc. Am. B* **22**, 1939 (2005)