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# Photophysical Characterization, Two-Photon Absorption and Optical Power Limiting of Two Fluorenylperylene Diimides

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Perylene diimides have unique optical and electronic properties and have attracted interest in fields ranging from nonlinear optics to photovoltaics. The steady-state linear photophysical properties, two-photon absorption (2PA) spectra, and optical limiting behavior of fluorenylperylene diimide-based derivatives were investigated in solution at room temperature. An efficient intramolecular energy transfer and specific strong dependences of fluorescence quantum yield on solvent properties were observed. The 2PA spectra were measured over a broad spectral region by two-photon induced fluorescence and open aperture Z-scan methods under femtosecond and picosecond excitation, respectively. The maximum values of pure 2PA cross sections, up to  $\sim 3500$  GM, were obtained for fluorenylperylene diimide-based derivatives under picosecond excitation, when excited-state absorption and stimulated emission processes were taken into account. These perylene derivatives exhibited efficient two-photon optical power limiting under picosecond excitation.

## 1. Introduction

Perylene-based derivatives possess relatively unique photophysical and photochemical properties and have great potential for a number of applications, including photoinduced electron-transfer organic systems,<sup>1,2</sup> semiconducting materials for electrophotography,<sup>3,4</sup> organic photovoltaic devices for solar energy conversion,<sup>5–7</sup> and optoelectronic elements and photosensitizers.<sup>8–10</sup> The perylene moiety can exhibit electron-donor or electron-acceptor properties, depending on the nature of lateral substituents,<sup>11,12</sup> and are characterized by specific energy and charge-transfer processes in the excited state.<sup>2,13,14</sup> Certain perylene derivatives also exhibit self-assembling<sup>15,16</sup> and aggregation<sup>17</sup> properties, facilitating light harvesting and high efficiency energy transfer.<sup>18,19</sup> In some particular cases, because of its rigid-rod nature, perylene-based structures can serve as standards for steady-state fluorescence anisotropy.<sup>14</sup>

Investigation of the nonlinear-optical properties of perylene-based organic molecules<sup>20–21</sup> promises to expand their possible use and, therefore, is a subject of quite intensive research. For example, the investigation of two-photon absorption (2PA) properties of some perylene-based derivatives were performed by Mendonca et al.<sup>22–24</sup> by an open aperture Z-scan method.<sup>25</sup> A high 2PA cross section ( $\sim 3400$  GM) and two-photon optical limiting was reported for bis-(benzimidazo)perylene.<sup>23</sup> The results of this study provide impetus for further, comprehensive investigations of the linear and nonlinear optical properties of this important class of organic material.

In this work, we present linear photophysical and nonlinear optical properties of 2,9-bis(7-benzothiazole-9,9-didecylfluoren-2-yl)perylene diimide (**1**) and 2,9-bis(7-diphenylamino-9,9-didecylfluoren-2-yl)perylene diimide (**2**), two perylene diimide derivatives with very different electronic character of the imide substituents. Strong specific dependence of the fluorescence

quantum yield on the solvent properties was shown for **1**, a derivative with electron deficient fluorenyl moieties, and was similar to the corresponding behavior of 2,7-bis(*N*-(1-hexylheptyl)-3,4:9,10-perylene-bisimide-*N'*-yl)-9,9-didodecylfluorene (PFP).<sup>2</sup> Two-photon absorption spectra of **1** and **2** were obtained over a broad spectral range by two separate methodologies: the two-photon induced fluorescence (2PF) method<sup>26</sup> and open aperture Z-scan method with a recently modified fitting procedure.<sup>27</sup> The effect of two-photon optical limiting for **1** and **2** was demonstrated under picosecond excitation.

## 2. Experimental Section

The synthesis of the fluorenylperylene diimide-based derivatives **1** and **2** was described previously,<sup>28</sup> and their molecular structures are presented in Figure 1. All linear photophysical parameters were measured in spectroscopic grade toluene, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and *o*-dichlorobenzene (ODCB). The absorption spectra were recorded with an Agilent 8453 UV–visible spectrophotometer in 0.1 mm, 1 mm, and 10 mm path length quartz cuvettes for the range of dye concentrations  $2.4 \times 10^{-3} \leq C \leq 10^{-6}$  M. The steady-state fluorescence, excitation, and excitation anisotropy spectra were obtained at room temperature with PTI QuantaMaster spectrofluorimeter in 10 mm spectrofluorometric quartz cuvettes with dye concentrations  $\sim 10^{-6}$  M. All fluorescence spectra were corrected for the spectral dependence of the emission monochromator and PMT. The fluorescence quantum yields of **1** and **2** were determined in single solvents and binary solvent mixtures, toluene–CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>–ODCB, relative to Rhodamine 6G in ethanol at room temperature.<sup>29</sup> The dielectric constant,  $\epsilon$ , and refractive index,  $n$ , for the solutions were determined from the corresponding values of the constituent solvents and the relative proportion of each solvent (“rule of mixtures” approach<sup>30</sup>). These measurements were performed to probe the solvent dependence of the fluorescence quantum yields of **1** and **2**.

Two-photon absorption (2PA) spectra of **1** and **2** were measured in spectroscopic grade toluene and CH<sub>2</sub>Cl<sub>2</sub> over a

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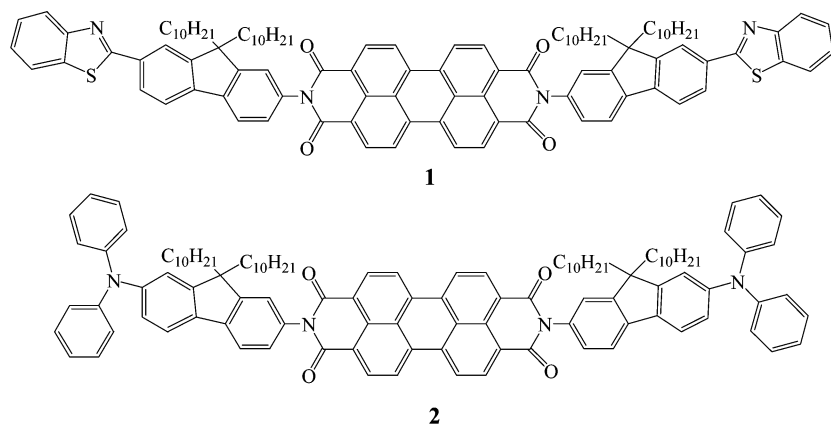


Figure 1. Molecular structures of compounds **1** and **2**.

TABLE 1: Values of Absorption,  $\lambda_{abs}^{max}$ , and Fluorescence,  $\lambda_{fl}^{max}$ , Maxima, Fluorescence Quantum Yields,  $\Phi$ , and Extinction Coefficients,  $\epsilon^{max}$ , for **1** and **2** in Toluene and  $CH_2Cl_2$

solvent	<b>1</b>		<b>2</b>	
	toluene	$CH_2Cl_2$	toluene	$CH_2Cl_2$
$\lambda_{abs}^{max}$ , nm	529 $\pm$ 1	528 $\pm$ 1	528 $\pm$ 1	527 $\pm$ 1
$\lambda_{fl}^{max}$ , nm	536 $\pm$ 1	533 $\pm$ 1	533 $\pm$ 1	531 $\pm$ 1
$\Phi$	0.23 $\pm$ 0.03	(2.5 $\pm$ 0.8) $\times 10^{-3}$	(6 $\pm$ 3) $\times 10^{-5}$	(1.2 $\pm$ 0.4) $\times 10^{-4}$
$\epsilon^{max} \times 10^{-3}$ , M $^{-1}$ ·cm $^{-1}$	98 $\pm$ 10	130 $\pm$ 10	90 $\pm$ 10	120 $\pm$ 10

broad spectral region by two separate methods in order to increase the validity of the experimental data. The first method was the relative 2PF method with fluorescein in water (pH = 11) and Rhodamine B in methanol as standards.<sup>26</sup> A PTI QuantaMaster spectrofluorimeter was used while a Clark-MXR CPA-2001 femtosecond laser pumped an optical parametric generator/amplifiers (TOPAS, Light Conversion), with pulse duration,  $\approx 140$  fs, (FWHM), 1 kHz, repetition rate, tuning range 660–1060 nm, and pulse energies  $0.05 \mu J \leq E_p \leq 0.15 \mu J$  served as the excitation source. These measurements were performed in 10 mm spectrofluorometric quartz cuvettes with dye concentrations  $\sim 5 \times 10^{-5}$  M. Possible reabsorption of fluorescence emission was analyzed and taken into account. The quadratic dependence of two-photon induced fluorescence intensity on the excitation power was checked for each excitation wavelength.

The second method for the determination of 2PA spectra of **1** and **2** was an open aperture Z-scan method based on well-known experimental methodology,<sup>25</sup> with a modified fitting procedure that took into account excited-state absorption and stimulated emission processes.<sup>27</sup> These measurements were performed in 1 mm path length quartz cuvettes with dye concentrations  $\sim (1.5\text{--}2.5) \times 10^{-3}$  M. For the Z-scan 2PA measurements, a picosecond Nd:YAG laser (PL 2143 B Ekspla) coupled to an optical parametric generator (OPG 401/SH) was used. The excitation laser beam with pulse duration  $\approx 35$  ps (FWHM), pulse energies  $0.05 \mu J \leq E_p \leq 5 \mu J$ , and repetition rate 10 Hz was tuned over the spectral range 640–1060 nm.

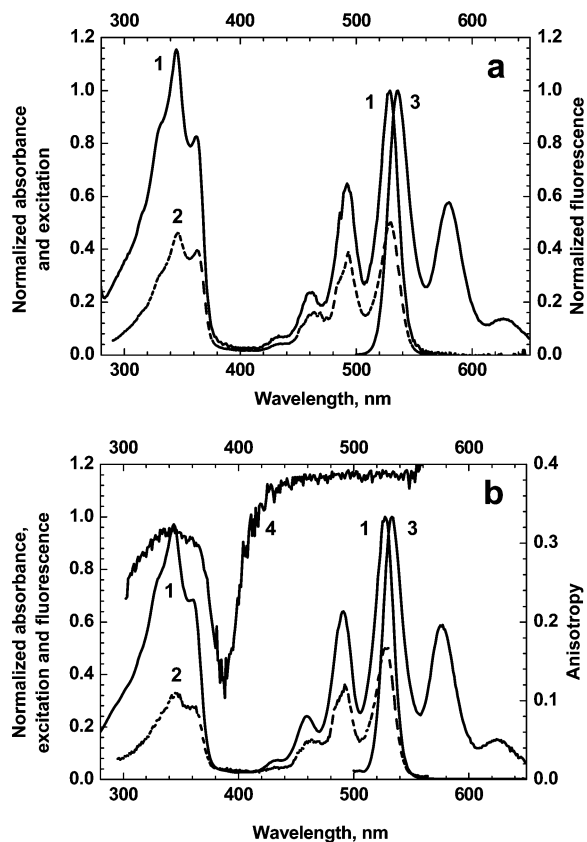
Two-photon optical power limiting effects were shown for **1** and **2** in  $CH_2Cl_2$  with the same picosecond laser beam focused to a waist of radius 25  $\mu m$ , for excitation wavelength 660 nm and pulse energies up to 10  $\mu J$ . These measurements were performed in 1 mm path length quartz cuvettes with dye concentrations  $\sim 2.4 \times 10^{-3}$  M.

### 3. Results and Discussion

**3.1. Linear Photophysical Properties.** Perylene diimides **1** and **2** (Figure 1) consist of two different chromophore systems: one consisting of a perylene diimide core and the other

one consisting of electron donating or accepting-substituted fluorenyl terminal groups. The main photophysical characteristics of these compounds are shown in Table 1 and Figures 2 and 3. The absorption spectra of **1** and **2** (Figures 2, 3, curves 1) exhibit two intense absorption bands in the UV–visible region, corresponding to the perylene and fluorene chromophores. The shape and spectral position of these bands (see Table 1) are close to the corresponding parameters for separate perylene diimide<sup>24</sup> and fluorene derivatives with diphenylamino and benzothiazole end substituents.<sup>31</sup> This indicates only a weak electronic coupling between the two different chromophore systems. The excitation spectra of **1** and **2** in toluene and  $CH_2Cl_2$  (Figures 2 and 3, curve 2) were similar to the corresponding absorption bands (curve 1). This is consistent with efficient intramolecular energy transfer from the fluorenyl group to the perylene ring system after excitation in the short wavelength absorption band. Taking into account the spectral characteristics of **1** and **2** and the relatively short distance between two chromophore systems ( $\sim 10$  Å), an intramolecular Förster resonance energy transfer mechanism<sup>29</sup> can be assumed for this process, which can be competitive to vibrational relaxation pathways in accordance with Kasha's rule.<sup>32</sup>

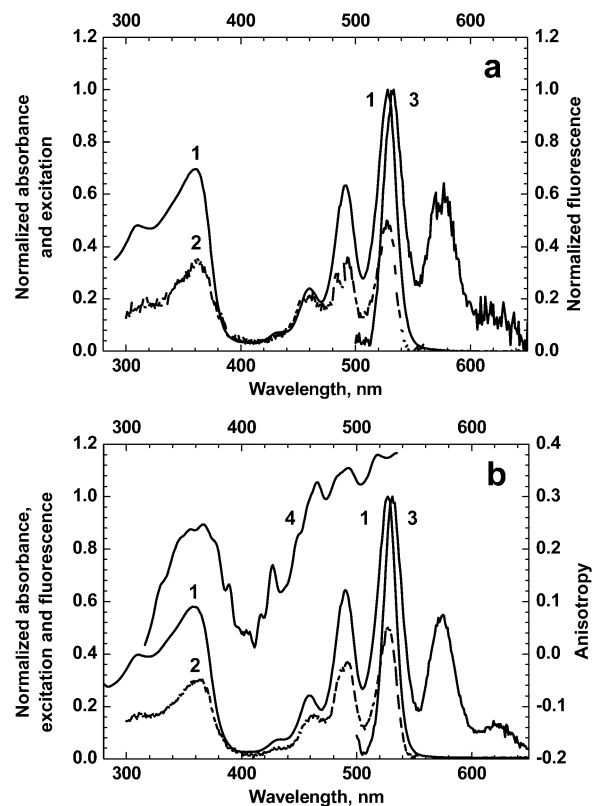
Excitation anisotropy spectra (Figures 2 and 3, curve 4) reveal the spectral position and relative orientation of the main transition dipoles in **1** and **2**. In general, the value of steady-state fluorescence anisotropy,  $r$ , can be expressed through the angle,  $\alpha$ , between absorption and emission dipoles as<sup>29</sup>  $r = (3 \cdot \cos^2 \alpha - 1)/5$ . A high value of  $r \approx 0.38$  in the main absorption band (440–540 nm) indicates a nearly parallel orientation of the absorption  $S_0 \rightarrow S_1$  and emission  $S_1 \rightarrow S_0$  transition dipoles ( $S_0$  and  $S_1$  are the ground and first excited electronic states, respectively). For this case, it is possible to determine the relative orientations of  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_n$  transition dipoles ( $S_n$  is a higher electronically excited state). From Figure 2, curve 4, the values of anisotropies  $r \approx 0.33$  in the fluorenyl absorption bands at 340–360 nm (curves 1) corresponds to an angle of  $\sim 20^\circ$  between the perylene and the fluorenyl chromophores in compound **1**. This is in good agreement with structures of **1** in Figure 1. The minimum value of anisotropy for **1** at  $\sim 380$ –



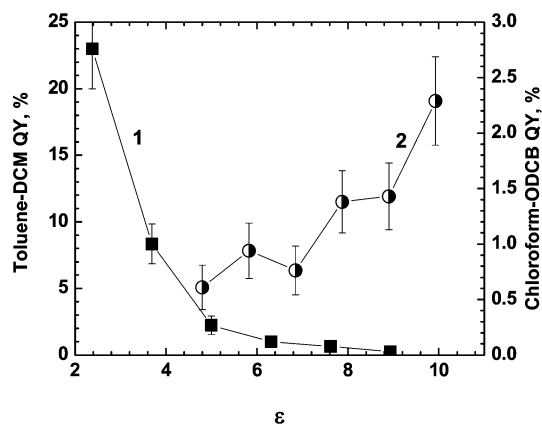
**Figure 2.** Normalized absorbance (1), excitation (2), fluorescence (3), and excitation anisotropy (4) spectra of **1** in toluene (a), CH<sub>2</sub>Cl<sub>2</sub> (b) and polyTHF (b, curve 4). Excitation spectra are normalized to 0.5 and obtained for observed wavelength 580 nm.

390 nm can be attributed to the second electronic absorption band of perylene diimide with transverse orientation of corresponding transition dipole. This band is relatively weak<sup>14</sup> and was not observed in the absorption spectrum of **1** (Figure 2, curve 1). The qualitative behavior of the excitation anisotropy for compound **2** is similar (Figure 3, curve 4), but quantitative estimations cannot be very accurate because of the extremely low fluorescence quantum yield  $\sim 10^{-4}$  (see Table 1).

All absorption, excitation, and fluorescence spectra of the two fluorenylperylenediimide derivatives were nearly independent of solvent (Figures 2 and 3). This is in stark contrast to their fluorescence quantum yields,  $\Phi$ , which exhibited strong and specific solvent dependences. In Figure 4, the dependences of  $\Phi$  on the static dielectric constant of the medium,  $\epsilon$ , are presented for **1** in mixtures of toluene–CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>–ODCB. It is reasonable to assume that the dielectric constant varies linearly with composition of the mixtures. From Figure 4, it can be seen that different types of solvents exhibit qualitatively different influences on the fluorescence quantum yield. The value of  $\Phi$  decreases with  $\epsilon$  in toluene–CH<sub>2</sub>Cl<sub>2</sub> mixtures and increases in mixtures of CHCl<sub>3</sub>–ODCB. Compound **2** exhibited the opposite and less pronounced dependence in toluene–CH<sub>2</sub>Cl<sub>2</sub>. The most reasonable explanation of this rather complex behavior of  $\Phi$  can be based on the “short-distance” electron-transfer mechanism comprehensively described in ref 2. According to this mechanism, an electron is transferred from a fluorenyl chromophore to the perylene diimide core in the S<sub>1</sub> state with a rate constant that is extremely sensitive to changes in solvent properties. As shown in ref 2, the rate constant for the intramolecular charge transfer can exhibit a rather complex (nonmonotonic) dependence on solvent polarity,  $\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$ , which is



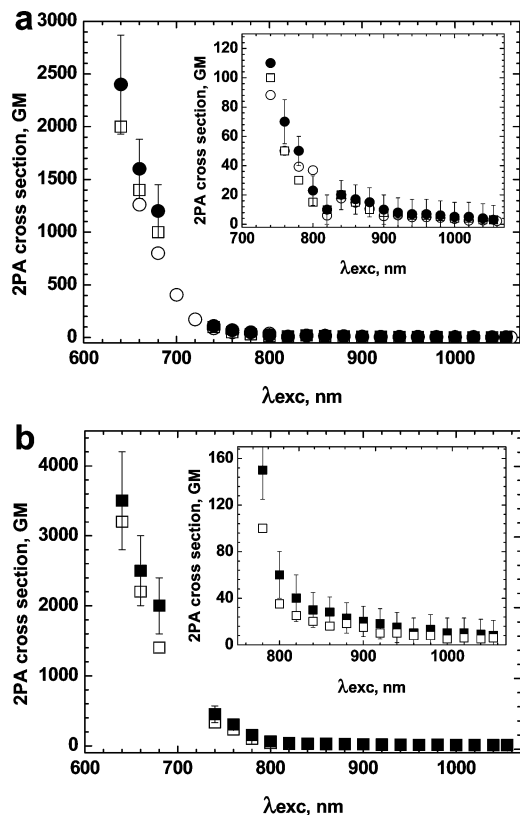
**Figure 3.** Normalized absorbance (1), excitation (2), fluorescence (3), and smoothed excitation anisotropy (4) spectra of **2** in toluene (a), CH<sub>2</sub>Cl<sub>2</sub> (b) and polyTHF (b, curve 4). Excitation spectra are normalized to 0.5 and obtained for observed wavelength 580 nm.



**Figure 4.** Dependences of the fluorescence quantum yield,  $\Phi$ , on the dielectric constant,  $\epsilon$ , of the solvent mixtures (0, 20, 40, 60, 80, and 100 volume %, respectively): toluene–CH<sub>2</sub>Cl<sub>2</sub> (1) and CHCl<sub>3</sub>–ODCB (2) for compound **1**.

a function not only of the static dielectric constant,  $\epsilon$ , but also on the refractive index of the medium,  $n$ . Therefore, different trends for the dependence  $\Phi = f(\epsilon)$  can be observed in different solvents. A large value of the electron-transfer rate constant of **1** in CH<sub>2</sub>Cl<sub>2</sub> is consistent with the assumption that the difference between oxidation potential of the fluorenyl group and the reduction potential of perylene bisimide in CH<sub>2</sub>Cl<sub>2</sub> corresponds to the energy of the first excited state of **1**.

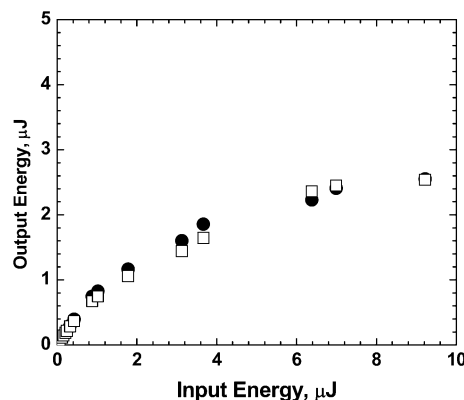
**3.2. Nonlinear-Optical Properties.** 2PA spectra of **1** and **2** obtained by 2PF and open aperture Z-scan methods over a broad spectral range are shown in Figure 5. The 2PF method was used only for compound **1** in toluene because of its relatively high fluorescence quantum yield ( $\Phi \approx 0.23$ ; see Table 1). In the range of excitation wavelengths,  $\lambda_{exc} \geq 640$  nm, linear absorp-



**Figure 5.** (a) 2PA spectra of **1** in toluene ( $\circ$ ,  $\square$ ) and  $\text{CH}_2\text{Cl}_2$  ( $\bullet$ ,  $\blacksquare$ ) obtained by 2PF ( $\circ$ ) and open aperture Z scan ( $\square$ ,  $\bullet$ ) methods; (b) 2PA spectra of **2** in toluene ( $\square$ ) and  $\text{CH}_2\text{Cl}_2$  ( $\blacksquare$ ) obtained by open aperture Z-scan method. Insets are expansions of the lower energy region.

tion was neglected for all of the solutions along with one-photon nonlinear absorption processes from the ground state which can affect the accuracy of 2PA measurements. As deduced from Figure 5a, the results of both methods were in good agreement with each other. The values of 2PA cross section reached their maximum of 2000–2500 GM for **1** and 3000–3500 GM for **2** at the shortest  $\lambda_{\text{exc}}$  and decreased monotonically in the long wavelength direction. No separate absorption maxima related to the spectral position of two-photon allowed absorption bands were observed in the spectral range 640–1055 nm. The shoulder at 840 nm in the 2PA spectra of **1** (Figure 5a) was not resolvable from the error bars. Dramatic enhancement of the 2PA cross section in the short wavelength range can be explained by intermediate-state resonant enhancement<sup>33,34</sup> related to the decrease in detuning energy between incident photons and the lowest one-photon allowed state. All 2PA spectra were similar to the corresponding ones for perylene tetracarboxylic derivatives<sup>24</sup> except for the maxima values of 2PA cross sections. The discrepancy of 2–3 fold related to the modified fitting methodology takes into account excited-state absorption and stimulated emission processes. 2PA under excitation into the main absorption band of **1** and **2** ( $\lambda_{\text{exc}} = 1055$  nm) was relatively small because of the symmetrical structure of the perylene diimide moiety and was consistent with the quantum mechanical selection rules in which two-photon transitions are strictly forbidden for this transition.<sup>35</sup>

Optical power limiting, the optical analog to an electrical surge protector, is important for the protection of optical sensors and eyes from sudden exposure to high incident intensities. Any materials that undergo an efficient nonlinear absorption response as a function of incident intensity are of great interest for optical power limiting. Two-photon optical power limiting was inves-



**Figure 6.** Output energy as a function of the input energy for **1** ( $\bullet$ ) and **2** ( $\square$ ) in  $\text{CH}_2\text{Cl}_2$  under picosecond excitation at  $\lambda_{\text{exc}} = 660$  nm, in 1 mm quartz cuvettes with dye concentrations  $\sim 2.5 \times 10^{-3}$  M. The absolute accuracy of each point is  $\pm 10\%$ .

tigated for **1** and **2** in  $\text{CH}_2\text{Cl}_2$  under picosecond excitation and is shown in Figure 6. High values of 2PA cross sections at  $\lambda_{\text{exc}} = 660$  nm, along with excited-state absorption, resulted in a relatively strong optical power limiting effect obtained under two-photon excitation (in 1 mm quartz cuvette with molecular concentrations  $\sim 2.4 \times 10^{-3}$  M). By taking into account the difference in 2PA cross sections for **1** and **2** in  $\text{CH}_2\text{Cl}_2$  at  $\lambda_{\text{exc}} = 660$  nm, nearly the same limiting effect for **1** and **2** can be explained by a more efficient excited-state absorption for compound **1**. The figure of merit,  $M = T_0/T_H$  ( $T_0$  and  $T_H$  are the transmittances at low and highest intensity, respectively),<sup>36</sup> for optical limiting properties of **1** and **2** under picosecond excitation ( $M \approx 3.5$ ) is comparable to fluorene-based polymetallaynes under nanosecond excitation ( $M \approx 4\text{--}4.5$ )<sup>37</sup> and exceeds the efficiency of multi-branched fluorene-based chromophores in the femtosecond regime ( $M \approx 1.5$ ).<sup>38</sup> This suggests derivatives such as **1** and **2** may be useful for the development of new multifunctional organic materials for two-photon based optical power limiting.

## Conclusions

The steady-state photophysical properties of fluorenylperylene diimide-based derivatives **1** and **2** were investigated in toluene and  $\text{CH}_2\text{Cl}_2$ . An efficient energy transfer from the terminal fluorenyl group to the central perylene diimide core was observed. The nature of this process can be based on the Förster's resonance energy transfer mechanism. The fluorescence quantum yield of **1** exhibited a strong specific solvent dependence. The value of  $\Phi$  in toluene– $\text{CH}_2\text{Cl}_2$  mixtures decreased by nearly 2 orders of magnitude with an increase in the dielectric constant of the medium from 2.4 to 8.9. Interestingly, a reverse and less pronounced dependence was observed for **1** in  $\text{CHCl}_3$ –ODCB mixtures.

The 2PA spectra of **1** and **2** were obtained over a broad spectral region (640–1055 nm) by femtosecond 2PF and picosecond open aperture Z-scan methods, by taking into account excited-state absorption and stimulated emission processes. The results of both methods were in good agreement with each other. Compounds **1** and **2** exhibited maxima 2PA absorption cross sections (up to 3500 GM) at short wavelength excitation,  $\lambda_{\text{exc}} = 640$  nm, and a monotonic decrease in their 2PA cross section values progressing to longer wavelengths. No distinctly separate peaks in the 2PA spectra were observed for the two perylene diimide derivatives. The effect of two-photon optical power limiting was demonstrated for both **1** and **2** in  $\text{CH}_2\text{Cl}_2$  under picosecond excitation. The specific steady-



state photophysical properties, high 2PA cross sections, and two-photon optical limiting abilities of **1** and **2** strongly suggest their utility in a number of nonlinear optical applications, including optical power limiting and data storage, subjects of more detailed investigations in the future.

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## References and Notes

- (1) Weiss, E. A.; Sinks, L. E.; Lukas, A. S.; Chernick, E. T.; Ratner, M. A.; Wasielewski, M. R. *J. Phys. Chem. B* **2004**, *108*, 10309.
- (2) Neuteboom, E. E.; Meskers, S. C. J.; Beckers, E. H. A.; Chopin, S.; Janssen, R. A. J. *J. Phys. Chem. A* **2006**, *110*, 12363.
- (3) Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449.
- (4) Borsenberger, P. M.; Weiss, D. S. *Organic Photoreceptors for Xerography*; Marcel Dekker: New York, 1998.
- (5) Hiramoto, M.; Ihara, K.; Fukusumi, H.; Yokoyama, M. *J. Appl. Phys.* **1995**, *78*, 7153.
- (6) Shibano, Y.; Umeiyama, T.; Matano, Y.; Imahori, H. *Org. Lett.* **2007**, *9*, 1971.
- (7) Li, J.; Dierschke, F.; Wu, J.; Grimsdale, A. C.; Müllen, K. *J. Mater. Chem.* **2006**, *16*, 96.
- (8) Schmidt, A.; Schuerlein, T. J.; Collins, G. E.; Armstrong, N. R. *J. Phys. Chem.* **1995**, *99*, 11770.
- (9) Gomez, U.; Leonhardt, M.; Port, H.; Wolf, H. C. *Chem. Phys. Lett.* **1997**, *268*, 1.
- (10) Icli, S.; Demica, S.; Dindar, B.; Doroshenko, A. O.; Timur, C. J. *Photochem. Photobiol. A* **2000**, *136*, 15.
- (11) Horowitz, G.; Kouki, F.; Spearman, P.; Fichou, D.; Nogues, C.; Pan, X.; Garnier, F. *Adv. Mater.* **1996**, *8*, 242.
- (12) Weil, T.; Wiesler, U. M.; Herrmann, A.; Bauer, R.; Hofkens, J.; De Schryver, F. C.; Müllen, K. *J. Am. Chem. Soc.* **2001**, *123*, 8101.
- (13) Just, E. M.; Wasielewski, M. R. *Superlattices Microstruct.* **2000**, *28*, 317.
- (14) Belfield, K. D.; Bondar, M. V.; Przhonska, O. V.; Schafer, K. J. *J. Photochem. Photobiol. A* **2002**, *151*, 7.
- (15) Ishii, T.; Murakami, K.; Imai, Y.; Mataka, S. *Org. Lett.* **2005**, *7*, 3175.
- (16) Balakrishnan, K.; Datar, A.; Naddo, T.; Huang, J.; Oitker, R.; Yen, M.; Zhao, J.; Zang, L. *J. Am. Chem. Soc.* **2006**, *128*, 7390.
- (17) Sapagovas, V. J.; Gaidelis, V.; Kovalevskij, V.; Undzenas, A. *Dyes Pigments* **2006**, *71*, 178.
- (18) Kuhlbrandt, W.; Wang, D. N.; Fujiyoshi, Y. *Nature* **1994**, *367*, 614.
- (19) McDermott, G.; Prince, S. M.; Freer, A. A.; Hawthornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaacs, N. W. *Nature* **1995**, *374*, 517.
- (20) Cui, S.; Jiang, L.; Li, Y.; Huang, C.; Shi, G.; Liu, H.; Li, J.; Li, C.; Song, Y.; Gan, L.; Zhu, D. *Thin Solid Films* **2007**, *515*, 7140.
- (21) Fuller, M. J.; Wasielewski, M. R. *J. Phys. Chem. B* **2001**, *105*, 7216.
- (22) De Boni, L.; Constantino, C. J. L.; Misoguti, L.; Aroca, R. F.; Zilio, S. C.; Mendonça, C. R. *Chem. Phys. Lett.* **2003**, *371*, 744.
- (23) Oliveira, S. L.; Corrêa, D. S.; Misoguti, L.; Constantino, C. J. L.; Aroca, R. F.; Zilio, S. C.; Mendonça, C. R. *Adv. Mater.* **2005**, *17*, 1890.
- (24) Corrêa, D. S.; Oliveira, S. L.; Misoguti, L.; Zilio, S. C.; Aroca, R. F.; Constantino, C. J. L.; Mendonça, C. R. *J. Phys. Chem. A* **2006**, *110*, 6433.
- (25) Sheik-Bahae, M.; Said, A. A.; Wei, T. H.; Hagan, D. J.; Van Stryland, E. W. *IEEE Quant. Electron.* **1990**, *QE-26*, 760.
- (26) Xu, C.; Webb, W. W. *J. Opt. Soc. Am. B* **1996**, *13*, 481.
- (27) Belfield, K. D.; Bondar, M. V.; Hernandez, F. E.; Przhonska, O. V.; Yao, S. *J. Phys. Chem. B* **2007**, *111*, 12723.
- (28) Belfield, K. D.; Schafer, K. J.; Alexander, Jr. M. D. *Chem. Mater.* **2000**, *12*, 1184.
- (29) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Kluwer Academic/Plenum: New York, 1999.
- (30) Baur, J. W.; Alexander, M. D.; Banach, J. M.; Denny, L. R.; Reinhardt, B. A.; Vaia, R. A.; Fleitz, P. A.; Kirkpatrick, S. M. *Chem. Mater.* **1999**, *11*, 2899.
- (31) Belfield, K. D.; Bondar, M. V.; Przhonska, O. V.; Schafer, K. J. *J. Fluorescence* **2002**, *12*, 449.
- (32) Birks, J. B. *Organic Molecular Photophysics. Volume 1*; John Wiley & Sons: New York, 1973; p 16.
- (33) Kogej, T.; Beljonne, D.; Meyers, F.; Perry, J. W.; Marder, S. R.; Bredas, J. L. *Chem. Phys. Lett.* **1998**, *298*, 1.
- (34) Hales, J. M.; Hagan, D. J.; Van Stryland, E. W.; Schafer, K. J.; Morales, A. R.; Belfield, K. D.; Pacher, P.; Kwon, O.; Zojer, E.; Bredas, J. L. *J. Chem. Phys.* **2004**, *121*, 3152.
- (35) Peticolas, W. L. *Ann. Rev. Phys. Chem.* **1967**, *18*, 233.
- (36) Hagan, D. J.; Xia, T.; Said, A. A.; Wei, T. H.; Van Stryland, E. W. *Int. J. Nonlin. Opt. Phys.* **1993**, *2*, 483.
- (37) Zhou, G. J.; Wong, W. Y.; Ye, C.; Lin, Z. *Adv. Funct. Mater.* **2007**, *17*, 963.
- (38) Lin, T. C.; He, G. S.; Zheng, Q.; Prasad, P. N. *J. Mater. Chem.* **2006**, *16*, 2490.