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Effect of Host Substitution on Photochemical Properties of Pyrene/ β -Cyclodextrin Solid Complexes

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Pyrene/ β -cyclodextrin solid complexes (prepared using β -cyclodextrin, hydroxypropyl- β -cyclodextrin, and 2,3,6-triacetyl- β -cyclodextrin as hosts) were characterized by means of fluorescence spectroscopy and time-resolved diffuse reflectance laser flash photolysis. The relative intensity of the 0–0 and 0–2 vibronic bands in the emission spectrum of pyrene is found to increase as substitution of the cyclodextrin hydroxyl groups increases. Furthermore, a concomitant shortening in pyrene triplet lifetime results. Interestingly, a significant decrease in pyrene radical anion yield and lifetime is observed with 2,3,6-triacetyl- β -cyclodextrin as host; this effect is ascribed to the potential ability of the host matrix to trap electrons.

Keywords: Polarity; Fluorescent probe; Radical ion

INTRODUCTION

Cyclodextrins (CDs), naturally occurring cyclic oligosaccharides of six to eight α -D-glucose units, have been extensively studied over the course of past decades as molecular hosts for a large variety of guest molecules and ions [1,2]. Numerous substituted CDs have also been prepared and investigated to improve complex formation, host selectivity, or catalytic properties [3]. CDs are of particular interest as hosts to examine the photophysical and photochemical properties of guest species, as these can be (significantly) altered upon inclusion in host molecules [4]. Changes in guest properties are typically related to the 'polarity' immediately surrounding the guest species in these complexes, and to the physical constraints imposed to the molecular motion of the guest species by the host.

A common method used to determine local polarity in heterogeneous systems [5] (as well as in homogenous solvents [6]) is the measurement of pyrene (Py) fluorescence intensity of the 0–0 and 0–2 vibronic bands in the emission spectrum, which are ultimately related to the microscopic polarity around Py [7]. Although Py has been extensively used as a fluorescent probe to characterize CDs complexes in solution [8–14], studies on CD–Py complexes in the solid state are fairly scarce [15–17].

The present paper reports on the characterization of CD–Py solid complexes by means of fluorescence spectroscopy and time-resolved diffuse reflectance laser flash photolysis, using β -cyclodextrin (BCD), hydroxypropyl- β -cyclodextrin (HPCD), and 2,3,6-triacetyl- β -cyclodextrin (TACD) as hosts. The effects of host substitution on the relative intensity of the vibronic bands in the emission spectrum of Py, and on the yield and decay of Py photoinduced transient intermediates are presented.

RESULTS AND DISCUSSION

Formation of CD–Py solid complexes (prepared by either the two-layer precipitation method or slow solvent evaporation) was corroborated by means of differential scanning calorimetry (DSC) analysis (Figs. 1–3). Py crystals show an endothermic peak at about 150°C (curve A, Figs. 1–3), i.e. the Py melting temperature. On the DSC curves of BCD and HPCD, the peaks corresponding to the evaporation of water appear in the temperature range of 50–150°C (curve B, Figs. 1 and 2), while the DSC curve of TACD (curve B, Fig. 3) exhibits an endothermic peak at *ca.*

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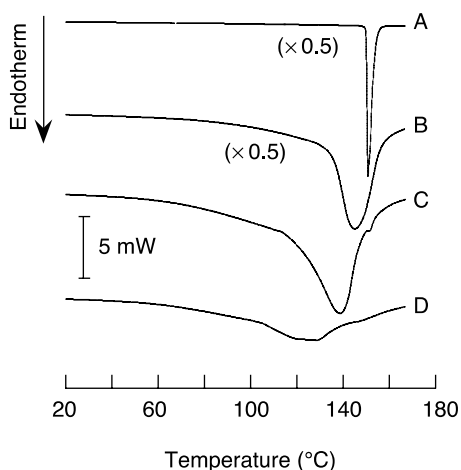


FIGURE 1 DSC thermograms of (A) Py, (B) BCD, (C) Py + BCD (physical mixture), (D) BCD-Py complex (two-layer precipitation method).

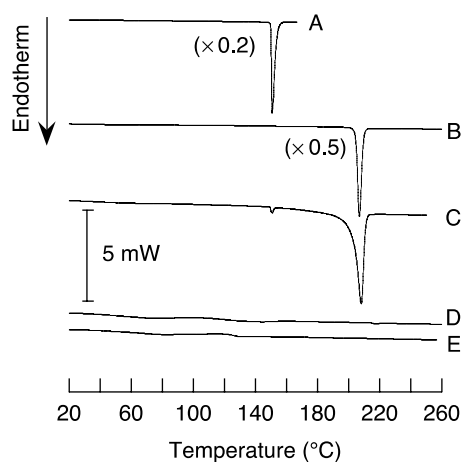


FIGURE 3 DSC thermograms of (A) Py, (B) TACD, (C) Py + TACD (physical mixture), (D) TACD-Py complex (slow-evaporation method, benzene as solvent), (e) TACD-Py complex (slow-evaporation method, dichloromethane as solvent).

207°C, i.e. the CD melting temperature. With all three CDs, the appearance of a minor peak corresponding to Py melting is evident in the DSC pattern of the physical mixtures (curve C, Figs. 1–3), whereas the Py fusion peak completely disappears in the two-layer precipitation and slow solvent evaporation samples (curves D–E, Figs. 1–3). This would indicate an almost complete loss of crystallinity of the binary system, a typical consequence of complexation [18].

Figure 4 shows the resulting steady-state fluorescence spectra for three different CD-Py solid complexes. Interestingly, the fluorescence intensity of the 0–0 (I_1) and 0–2 (I_3) vibronic bands vary with the type of CD. As clearly indicated in Fig. 4, the resulting I_1/I_3 ratios (average of three determinations) are found to increase in the order BCD < HPCD < TACD. The obtained value for BCD (0.45 ± 0.06) agrees well with the value previously reported (0.42) [15]. Values for HPCD (0.66 ± 0.03)

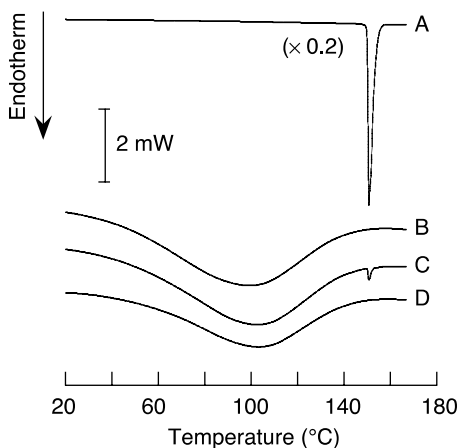


FIGURE 2 DSC thermograms of (A) Py, (B) HPCD, (C) Py + HPCD (physical mixture), (D) HPCD-Py complex (slow-evaporation method, ethanol as solvent).

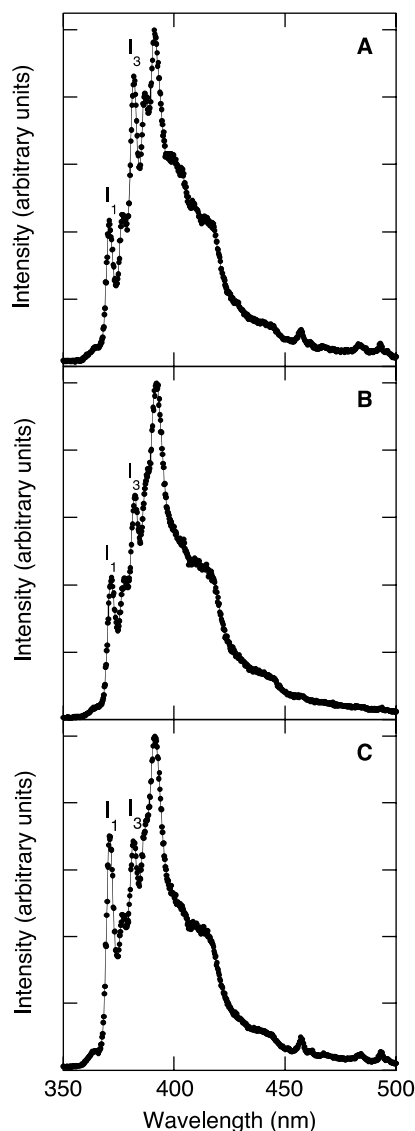


FIGURE 4 Fluorescence spectra of CD-Py complexes: (A) BCD, (B) HPCD, (C) TACD.

and TACD (0.99 ± 0.03) are comparable, respectively, to 1-octene and *o*-xylene environments [6].

The I_1/I_3 ratio for Py has been shown to increase with increasing solvent dipole-solute induced dipole interactions, and to be relatively insensitive to the hydrogen bonding capability of protic solvents [7]. Thus, based on the observed I_1/I_3 trend for CD solid complexes, one could conclude that the host-Py dipolar interactions increase in the order $\text{BCD} < \text{HPCD} < \text{TACD}$. It is interesting to note that the I_1/I_3 ratios reported for 1:1 and 2:1 BCD-Py complexes in aqueous solution (namely, 0.83 and 0.58, respectively [11]) are higher than the value for BCD-Py solid samples, consistent with a molecular environment that becomes considerably more hydrophobic. Furthermore, the larger I_1/I_3 ratios here reported for HPCD and TACD (relative to BCD) solid samples are consistent with the observation of higher Py I_1/I_3 values, in aqueous solution, in the presence of BCD derivatives relative to BCD [13].

BCD host molecules typically stack forming columns or channels [19]. Based on the I_1/I_3 trend mentioned above one could infer that penetration of Py in the cyclodextrin cavity increases in the order $\text{TACD} < \text{HPCD} < \text{BCD}$. In fact, guest molecules in TACD complexes have been shown to be accommodated in the matrix between the acyl chains, but not in the central cavity [20].

If the penetration of Py in the CD cavity increases as inferred above, one would anticipate a concomitant increase in Py triplet lifetime, owing to the restrictions imposed on conformation and mobility (as a consequence of the limited dimensions of the CD cavity and the rigidity of the probe molecule). Indeed, the 'less' polar CDs (i.e. BCD and HPCD) correspond to the complexes having longer-lived Py triplets than the 'more' polar TACD (see below).

Pulsed irradiation (at 355 nm) of CD-Py solid complexes leads, in all cases, to the formation of Py triplets and Py radical ions. Resulting time-resolved diffuse reflectance spectra are shown in Fig. 5. The bands at 420 and 520 nm are assigned to the triplet state of Py [21], the band at 450 nm to Py radical cation, and the band at 490 nm to Py radical anion [22]. The time-resolved spectra corresponding to BCD and HPCD solid complexes (Fig. 5a-b) largely retain their shape through time, i.e. all three Py transient species have quite comparable lifetimes. Interestingly, the time-resolved spectra for TACD solid complex (Fig. 5c) clearly indicate the presence of shorter-lived Py triplets and Py radical anions than in the case of BCD and HPCD solid samples. In addition, while the triplet-to-radical cation yield seems to be in general independent of the type of CD employed (average value, 1.36 ± 0.07), the triplet-to-radical anion yield for TACD (2.1 ± 0.1) is significantly higher than that for BCD or HPCD (average value, 1.3 ± 0.1). These 'yield ratios' were calculated

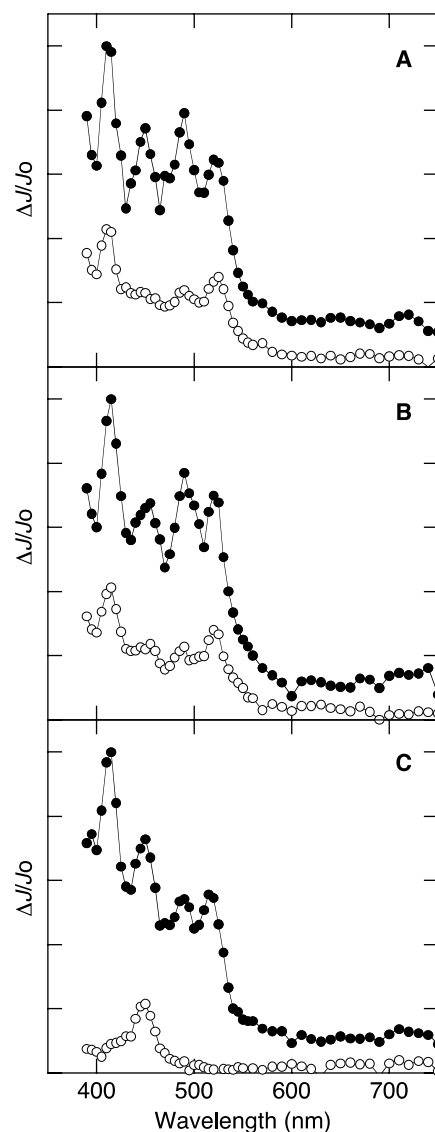


FIGURE 5 Time-resolved diffuse reflectance spectra for CD-Py complexes obtained $16 \mu\text{s}$ (filled diamonds) and $388 \mu\text{s}$ (open diamonds) after laser pulse. (A) BCD, (B) HPCD, (C) TACD.

by simply taking the ratio of signal intensities obtained at the wavelength of maximum absorption corresponding to each of the reactive intermediates involved (i.e. Py triplet, 420 nm; Py radical cation, 450 nm; Py radical anion, 490 nm) immediately after laser excitation. The formation of radical anions is thought to involve trapping of electrons ejected from excited singlet Py [15]. The fact that the yield and lifetime (see below) of Py radical anions in TACD solid samples are much lower than those in the other two CDs can be attributed to the fact that carbonyl groups are known to be good electron acceptors [23], thus, in the case of TACD complexes the host matrix would act as an 'electron sink'.

Figure 6 displays transient decay traces recorded, within $400 \mu\text{s}$ after laser excitation, at the wavelength of maximum absorption of each of the transient intermediates [24]. A two-exponential function

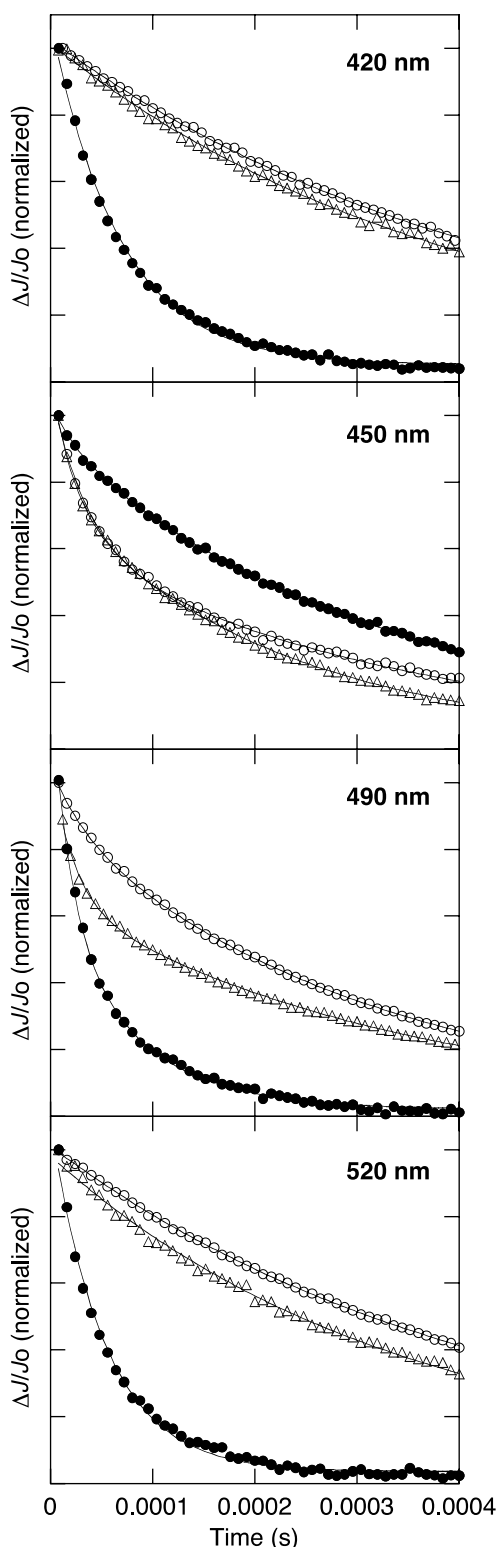


FIGURE 6 Normalized transient kinetic traces (recorded at a sampling rate of $4\mu\text{s}/\text{point}$) for CD-Py complexes: (open diamonds) BCD, (open triangles) HPCD, (filled diamonds) TACD. Traces monitored at 420 and 520nm were fitted to a mono-exponential function, while those recorded at 450 and 490 nm were fitted to a two-exponential function.

adequately describes the decay traces monitored at 450 and 490 nm (i.e. Py radical ions as main absorbing species), whereas a single exponential appears to be

suitable for describing Py triplet decays (i.e. traces recorded at 420 and 520 nm). The resulting Py triplet lifetimes (average of two to three determinations) for BCD, HPCD, and TACD solid samples are 420 ± 10 , 360 ± 30 , and $60 \pm 10\mu\text{s}$, respectively. Within experimental error, values for BCD and HPCD samples are essentially the same, but it is clear there is a significant shortening of Py triplet lifetime upon substitution (acetylation) of all BCD hydroxyl groups. An analysis of the source(s) determining this shortening in triplet lifetime (e.g. restrictions on probe mobility, ability of oxygen to diffuse to reaction site) awaits indeed further investigations; however, it should be mentioned that quenching by energy transfer seems an unlikely contributing factor, since Py triplet energy is much lower than that for typical triplet carbonyls [25].

As already mentioned, decay traces for Py radical ions are very well reproduced by a two-exponential function. The two resulting lifetimes for Py radical cations seem to be independent of the type of CD employed, with average values of 300 ± 40 and $27 \pm 4\mu\text{s}$. It is the relative contribution of these two lifetimes that seems to vary with the host; the percent contribution of the shorter-lived component of the fitting function decreases in the order BCD (44%) \geq HPCD (34%) \gg TACD (11%). Similar results are obtained for Py radical anions when lifetimes for BCD and HPCD solid samples are compared, i.e. the two lifetimes seem independent of the type of host (average values are 320 ± 10 and $27 \pm 5\mu\text{s}$). Interestingly, the percent contribution of the shorter-lived component of the fitting function increases in the order BCD (16%) $<$ HPCD (40%). As already pointed out, Py radical anions in TACD solid samples decay significantly faster than in the other two CDs. Resulting lifetimes, having essentially equal contributions to the fitting function, are 78 ± 2 and $19 \pm 1\mu\text{s}$. The shortening in Py radical anion lifetime is being ascribed to the (potential) ability of the host matrix to trap electrons. In this regard, it is interesting to note that while lifetime values for Py radical cations do not differ significantly between CDs, TACD samples are characterized by having the highest percentage of longer-lived Py radical cations (i.e. 89% for TACD vs. 56–66% for BCD and HPCD).

In summary, results presented here on CD solid supports show Py senses a less hydrophobic (indicated by the increase in Py I_1/I_3 ratio) and 'less restricted' (inferred from the decrease in Py triplet lifetime) environment, as substitution on the rim hydroxyl groups increases. The significant decrease in yield and lifetime of Py radical anions in TACD solid samples, ascribed to the potential ability of the host matrix to trap electrons, illustrates the active role CDs may play in CD supported photoreactions.

MATERIALS AND METHODS

β -Cyclodextrin, hydroxypropyl- β -cyclodextrin (molar substitution = 1.0), and 2,3,6-triacetyl- β -cyclodextrin (Aldrich) were used as received. Pyrene (Aldrich) was recrystallized twice from ethanol before use. Dimethylsulfoxide, dichloromethane, benzene (EM Science, Omnisolv grade), and diethyl ether (EM Science, ACS grade) were used as received. Water was purified by passage through a Millipore Milli-Q apparatus before use.

BCD-Py solid inclusion complexes were prepared in duplicate via the two-layer precipitation method (i.e. by precipitation from a saturated BCD aqueous solution layered underneath a concentrated Py solution in diethyl ether) [26]. This method rendered BCD-Py solid complexes with a host-to-guest mole ratio of *ca.* 7, value determined by means of UV-visible absorption spectroscopy using dimethylsulfoxide as a solvent, as reported in the literature [27]. All other CD solid complexes were prepared by duplicate via slow solvent evaporation [28], from a 7:1 (mole ratio) CD:Py solution in ethanol (HPCD), dichloromethane or benzene (TACD). All CD-Py physical mixtures were generated by grinding CD and Py (in a 7:1 mole ratio) in a mortar, for approximately 3–5 min.

Differential scanning calorimetry measurements were performed on a TA DSCQ100 differential scanning calorimeter with thermal analyzer. Samples were prepared by placing 4–8 mg of sample in sealed aluminium pans. The heating rate was 10°C/min over the 20–170°C (Py, BCD, HPCD) or 20–260°C (TACD) range under static air.

Room temperature fluorescence spectra were taken on a PTI QM-2 spectrofluorometer using 338 nm excitation. In all cases no excimer fluorescence was found. The intensity of the first (0–0) and third (0–2) vibronic peaks were measured, respectively, at 371 and 382 nm.

Laser experiments were carried out using an Nd/YAG laser (Continuum, Surelite I–10) operated at 355 nm (4–6 ns, <15 mJ/pulse) for excitation. Solid samples, contained in quartz cells constructed of 3 × 7 mm Suprasil tubing, were shaken after every laser pulse to ensure the irradiation of fresh portions of sample by each laser pulse. Further details on the time-resolved diffuse reflectance laser flash photolysis system employed in this study are reported elsewhere [15]. All measurements were carried out at 21 ± 1°C using air-equilibrated samples.

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References

- [1] Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer-Verlag: New York, 1977.
- [2] Szejtli, J. *Cyclodextrins and Their Inclusion Complexes*; Akadémiai Kiadó: Budapest, 1982.
- [3] Easton, C. J.; Lincoln, S. L. *Modified Cyclodextrins: Scaffolds and Templates for Supramolecular Chemistry*; Imperial College Press: London, 1999.
- [4] *Photochemistry in Organized and Constrained Media*; Rammamurthy, V., Ed.; VCH Publishers: New York, 1991.
- [5] Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press: New York, 1987.
- [6] Don, D. C.; Winnik, M. A. *Can. J. Chem.* **1984**, *62*, 2560.
- [7] Karpovich, D. S.; Blanchard, G. J. *J. Phys. Chem.* **1995**, *99*, 3951.
- [8] Kusumoto, Y. *Chem. Phys. Lett.* **1987**, *136*, 535.
- [9] Muñoz de la Peña, A.; Ndou, T.; Zung, J. B.; Warner, I. M. *J. Phys. Chem.* **1991**, *95*, 3330.
- [10] Matsui, K. *Langmuir* **1992**, *8*, 673.
- [11] Xu, W.; Demas, J. N.; DeGraff, B. A.; Whaley, M. J. *J. Phys. Chem.* **1993**, *97*, 6546.
- [12] Werner, T. C.; Colwell, K.; Agbaria, R. A.; Warner, I. M. *Appl. Spectrosc.* **1996**, *50*, 511.
- [13] Werner, T. C.; Forrestall, K. J.; McIntosh, S. L.; Pitha, J. *Appl. Spectrosc.* **2000**, *54*, 560.
- [14] Starukh, G. N.; Smirnova, N. P.; Eremenko, A. M.; Chuiko, A. A.; Abdel-Shafi, A. A.; Worrall, D. R.; Wilkison, F. *Theor. Exp. Chem.* **2001**, *37*, 103.
- [15] Barra, M.; Agha, K. A. *J. Photochem. Photobiol. A: Chem.* **1997**, *109*, 293.
- [16] Udachin, K. A.; Ripmeester, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 1080.
- [17] Takahashi, N.; Gombojav, B.; Yoshinari, T.; Nagasaka, S.; Takahashi, Y.; Yamamoto, T. G.; Kasuya, A. *J. Solid State Chem.* **2004**, *177*, 3479.
- [18] The dramatic decrease of the endothermic peak corresponding to TACD in the case of slow solvent evaporation samples is attributed to complex formation and sample amorphization.
- [19] Saenger, W. *Isr. J. Chem.* **1985**, *25*, 43.
- [20] Añibarro, M.; Gessler, K.; Usón, I.; Sheldrick, G. M.; Harata, K.; Uekama, K.; Hirayama, F.; Abe, Y.; Saenger, W. *J. Am. Chem. Soc.* **2001**, *123*, 11854.
- [21] Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.
- [22] Schomburg, H.; Streak, H.; Weller, A. *Chem. Phys. Lett.* **1973**, *22*, 1.
- [23] Afanassiev, A. M.; Okasaki, K.; Freeman, G. R. *Can. J. Chem.* **1979**, *57*, 839.
- [24] Similar experiments using CD-Py physical mixtures were unsuccessful, since strong sample emission prevented reliable measurements.
- [25] Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; pp. 3–35.
- [26] Saenger, W. *Angew. Chem. Int. Ed.* **1980**, *19*, 344.
- [27] Barra, M.; Bohne, C.; Scaiano, J. C. *Photochem. Photobiol.* **1991**, *54*, 1.
- [28] Szente, L. In *Comprehensive Supramolecular Chemistry*; Szejtli, J., Osa, T., Eds.; Elsevier: Oxford, 1996; vol. 3, pp. 243–252.