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Femtosecond Time-Resolved Photophysics of 1,4,5,8-Naphthalene Diimides

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The photophysical properties of a tetrahedral molecule with naphthalene diimide (NDI) moieties and of two model compounds were investigated. The absorption and fluorescence spectra of dialkyl-substituted NDI are in agreement with literature. While the absorption spectra of phenyl-substituted molecules are similar to all other NDIs, their fluorescence showed a broad band between 500 and 650 nm. This band is sensitive to the polarity of the solvent and is attributed to a CT state. The absorption spectra and lifetime (10 ± 2 ps) of the electronically excited singlet state of a dialkyl-substituted NDI was determined by femtosecond transient absorption spectroscopy, and the latter was confirmed by picosecond fluorescence spectroscopy. Nanosecond flash photolysis showed the subsequent formation of the triplet state. The presence of a phenyl substituent on the imide nitrogen of NDI resulted in faster deactivation of the singlet state (lifetime 0.5−1 ps). This is attributed to the formation of a short-lived CT state, which decays to the local triplet state. The faster deactivation was confirmed by fluorescence lifetime measurements in solution and in a low-temperature methyl-tetrahydrofuran glass.

Introduction

During the past decade research on organic electronics has grown enormously. Such organic electronics include organic field-effect transistors,[1−5] organic light-emitting diodes,[6−9] and all-organic photovoltaics.[10−12] This research is consistently in need of new types of conductive materials to improve their current efficiencies and deepen the understanding by checking general principles on wider classes of materials. These materials should be either of *p* or of *n*-type, with good electrochemical properties and an air-stable conductivity. Derivatives of 1,4,5,8-naphthalene diimides (NDIs) are known for such air-stable conductivity.[13] Due to this, NDIs have been used in the study of electron-transfer processes,[14−18] as liquid crystalline and photorefractive materials,[19−21] as photosynthetic model compounds,[22] and for opto-electronic applications.[23]

Electrochemical and photophysical properties of NDI have been explored previously by several groups. Penneau et al. have reported the dimerization and aggregation behavior of NDI radical anions in aqueous and DMF solutions based on extensive spectroscopic studies (UV−vis, NIR, IR, and ESR).[24] Photoprocesses of functionalized NDIs in aqueous media[25,26] and in the presence of DNA[27] were investigated together with the radical anion formation via photochemical mechanisms. Further investigations on the excited-state properties of NDI radical anions were carried out by Gosztola et al.[28]

Green et al. reported a detailed study on the photophysical properties of NDI by measuring both the fluorescence and phosphorescence, from which they calculated the singlet and triplet energy levels.[29] They attempted to measure the fluorescence lifetime of the NDI but found it too short to be determined accurately by their equipment, and therefore they estimated it to be <20 ps. The short singlet lifetime is attributed to fast depopulation of the singlet state via intersystem crossing. Following this report, Barros et al. undertook a systematic study on the absorption and fluorescence properties of NDI.[30] This study revealed that NDIs stack with aromatic solvents and give rise to exciplex fluorescence. In water, even at low concentrations, a red-shifted fluorescence was observed, which was attributed to ground-state aggregation of NDI. Although the triplet state and radical anion formation are well described in the above-mentioned reports, the singlet-state dynamics of NDIs have not yet been reported. Since the lifetime of the NDI singlet state has been reported to be <20 ps, it is necessary to do measurements in the femtosecond time domain to accurately determine the lifetime.

In a previous paper, we reported a novel NDI-based tetrahedral amorphous material that showed a high conductivity.[23] Though the conductivity of NDIs is not as high as that of other diimides with extended aromatic cores,[31] conductivities as high as 0.16 $cm^2 V^{-1} s^{-1}$ have been reported.[13] Since this material was intended for opto-electronic applications, such as organic photovoltaics, our interests also extend to the photophysical properties of this material. In this paper we report on the ultrafast excited-state dynamics of this tetrahedral molecule, **3**, and of two model compounds, **1** and **2** (Figure 1). In order to study their singlet-state dynamics, time-resolved techniques were applied, from the femtosecond to the nanosecond time domains. These studies reveal the singlet-state absorption and excited-state lifetimes and also delineate the deactivation pathways in dependence of the molecular structure. To the best of our

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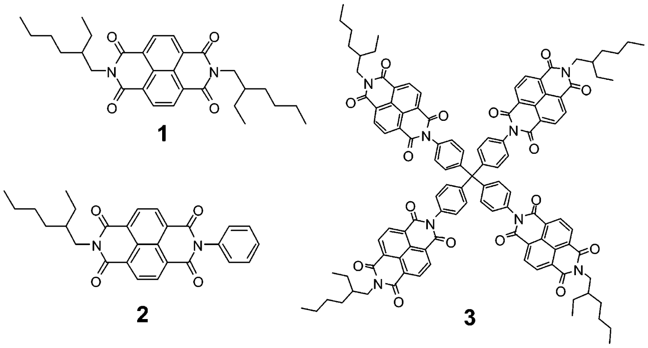


Figure 1. Structures of the naphthalene diimide derivatives under study.

knowledge, this is the first report of the NDI singlet-state absorption and of accurately determined lifetimes as measured with time-resolved techniques.

Experimental Section

General. The synthesis and characterization of the compounds used are described in detail elsewhere.[23] Steady-state absorption spectra were recorded with a Cary 100 UV−vis spectrophotometer. Fluorescence spectra were measured with a FLS 920 spectrophotometer (Edinburgh Instruments, U.K.) fitted with a red-sensitive PMT (R928, Hamamatsu). All the solvents used in this study are of spectrophotometric grade purchased from Sigma-Aldrich and were freshly distilled over drying agents before use.

Femtosecond Transient Absorption Measurements.[32] The pump beam was an ~100 fs laser pulse train out of an optical parametric amplifier (OPA) pumped by an amplified Ti:sapphire laser system (Spectra-Physics Hurricane) at a repetition rate of 1 kHz. Probing white light was produced by focusing a small amount of the fundamental beam (800 nm) on a sapphire plate. The probe beam was then focused on the sample such that the pump beam irradiated a larger area of the sample (~0.25 mm^2) compared to the probe beam (~0.1 mm^2) in order to guarantee a homogeneous optical density throughout the probing area. The transmitted light was collected by a photodiode. An Ocean Optics (Si, 2048 px) plug-in card diode array was used for the UV−visible region (200−1100 nm). The samples used for these measurements were prepared so that the absorbance of the samples was about 1 in a cuvette of 1 mm thickness. The solutions were continuously stirred during the measurements to minimize possible thermal effects and photodegradation. Roughly 350 transient absorption spectra were measured at different time delays. The increment between the consecutive spectra was increased during the experiment. The increment is 20 fs at early times and increases stepwise to 10 ps at the end of the experiment.

Global analyses of the transient absorption data were performed using Igor Pro, version 5.0.5A. In all cases three or four exponential functions convoluted with a Gaussian function representing the instrumental response were used to fit a data set.[33−35] The width of the Gaussian was fixed at the best value obtained from the fits at single wavelengths, and its value was about 200 fs (full width at half-maximum; fwhm) in all cases.

Picosecond Fluorescence Lifetime Measurements.[36] Fluorescence decay curves at single wavelengths were measured with picosecond time-correlated single-photon counting. The setup consisted of a mode-locked argon-ion laser (Coherent 486 AS mode locker and Coherent Innova 200 laser) which was used to pump a cavity dumped DCM dye-laser (Coherent model 700) synchronously. The output frequency was doubled with a BBO crystal, resulting in ~330 nm pulses. A Hamamatsu microchannel plate photomultiplier (R3809) was used as the detector. The Raman signal of water was taken as the instrument response function [fwhm ~ 18 ps].

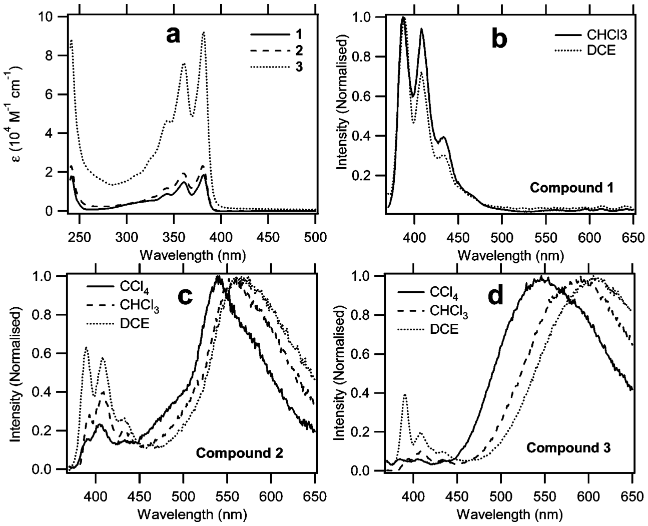


Figure 2. (a) Steady-state absorption spectra of **1**−**3** in chloroform and (b−d) fluorescence spectra of **1**, **2**, and **3**, respectively, in solvents of different polarity (λ_{exc} = 350 nm).

Fluorescence Lifetime Measurements at 77 K. Low-temperature fluorescence lifetime measurements were performed in a FLS 920 spectrophotometer (Edinburgh Instruments, U.K.) fitted with a cooled MCP PMT detector (Hamamatsu, R3809U-50). Samples were excited with a pulsed diode laser (LDH-P-C-375; PicoQuant GmbH, Germany; fwhm = 39 ps; λ_{exc} = 372 nm), controlled by a pulse controller (PDL 800-B; PicoQuant GmbH, Germany). The instrument response function (fwhm of IRF ~ 87 ps) was determined from scattering from colloidal silica Ludox (Sigma-Aldrich). The samples were cooled with a cryostat (Optistat DN; Oxford Instruments, U.K.), which was controlled with a temperature controller (ITC 503S; Oxford Instruments, U.K.).

Nanosecond Laser Flash Photolysis. Nanosecond laser flash photolysis studies were carried out using the third harmonic (355 nm, fwhm = 4 ns) of a Nd:YAG laser (Brilliant, Quantal Inc.). The transient spectra were obtained using an LP920 spectrophotometer (Edinburgh Instruments Limited) fitted with a 450 W Xe arc lamp as probe-light source and a red-sensitive photomultiplier (R928, Hamamatsu) and ICCD camera (DH720, Andor Technology) as detectors.

All spectroscopic measurements were carried out under magic-angle conditions, unless stated otherwise, to avoid the possible influence of rotational motions of the probe molecules.

Results and Discussion

Steady-State Absorption and Fluorescence Spectra. The steady-state absorption spectra of compounds **1**−**3** in chloroform (Figure 2a) have vibrational features with maxima at 344, 362, and 382 nm, and a high-energy band at 242 nm. They have high molar extinction coefficients (~10^4 M^{-1} cm^{-1}), indicating that the transition is $\pi-\pi^*$ in nature. The steady-state fluorescence spectra between 380 and 450 nm (Figure 2b) form mirror images of the absorption spectra with a small Stokes shift and reveal fluorescence from the singlet state. The absorption and fluorescence spectra of **1** are in agreement with literature reports for other naphthalene diimides.[29,30] In the case of **2** and **3** a second broad fluorescence band is observed which has a peak

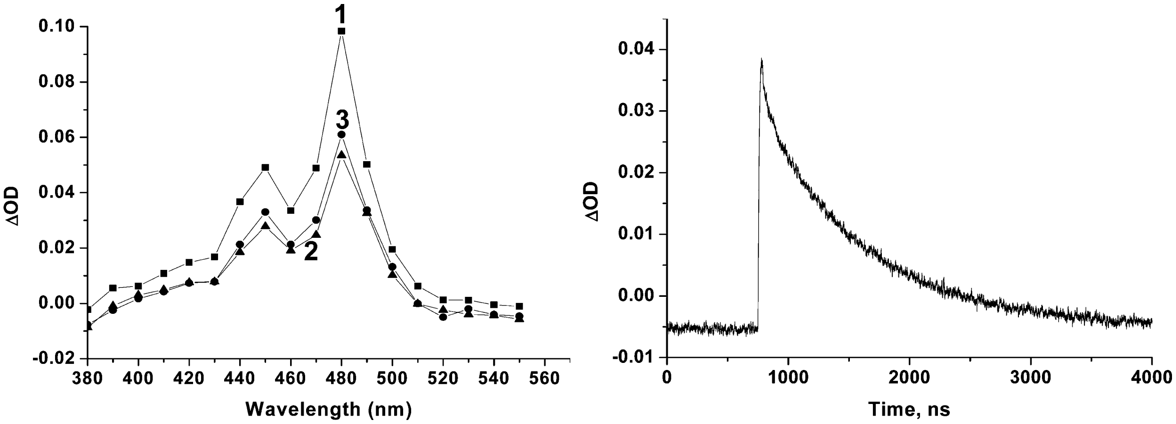


Figure 3. (left) Transient absorption spectra obtained with nanosecond laser flash photolysis experiments 40 ns after the pulse of **1** (square), **2** (triangle), and **3** (circle) in chloroform. (right) Representative decay curve of **3** at 480 nm (concentration ~ 10^{-5} M; $\lambda_{exc} = 355$ nm).

between 500 and 650 nm (Figure 2c,d). This band shifts to the red on increasing the polarity of the solvent (from tetrachloromethane to 1,2-dichloroethane), which suggests that it involves a partial transfer of charge. This charge-transfer (CT) band is interpreted to indicate that, in the case of **2** and **3**, there is an electron transfer between NDI and the phenyl ring. This is supported by the femtosecond transient absorption measurements (vide infra).

Nanosecond Transient Absorption Measurements. Laser flash photolysis experiments on a nanosecond time scale were done in chloroform for all three compounds, studied under aerated conditions. The spectra obtained are given in Figure 3. They show similar transient absorption spectra with two peaks at 450 and 480 nm.

These spectra are attributed to the triplet state of the naphthalene diimide.[23,29] The decays are monoexponential with lifetimes of 500, 450, and 900 ns for compounds **1**, **2**, and **3**, respectively. The extended triplet lifetime for compound **3** might be due to restriction in the rotational freedom of the chromophore imposed by the central tetraphenyl methane moiety. On this time scale, no other absorptions were observed than those of the triplet state within the spectral window employed (up to 800 nm). Femtosecond transient absorption measurements were performed to get more insight into the formation of the triplet state.

Femtosecond Transient Absorption Measurements. The time-resolved transient absorption spectra measured with femtosecond pump−probe experiments and the decay-associated difference spectra (DADS), obtained by global analysis of the data,[33,34] are depicted in Figure 4, together with the decay constants. In the transient spectra of **1** (Figure 4a), two distinct features are observed in time. Shortly after the pulse an absorption band with a maximum at 606 nm and a shoulder at 720 nm is present. This transient decays with a lifetime of 10 ± 2 ps and gives rise to a spectrum with absorption maxima at 456 and 488 nm. The DADS associated with the 10 ps decay shows a negative band at 488 nm, indicating a direct transition between these two transients.

The long-lived spectrum of **1** does not decay on the time scale of this experiment (up to 1 ns) and is similar to the triplet-state spectrum observed with nanosecond flash photolysis (vide supra). Therefore, this long-lived transient is attributed to the triplet state of NDI. The triplet state is formed directly from the short-lived species as indicated by DADS. So the transient at early times is most likely the singlet excited-state of NDI. To the best of our knowledge, this is the first report of the absorption spectrum and lifetime of the NDI singlet state as obtained from femtosecond transients. The photoprocesses of **1** are summarized in an energy level diagram given in Scheme 1. Upon excitation of **1** the singlet state is formed, which decays rapidly via intersystem crossing (ISC) to the triplet state.

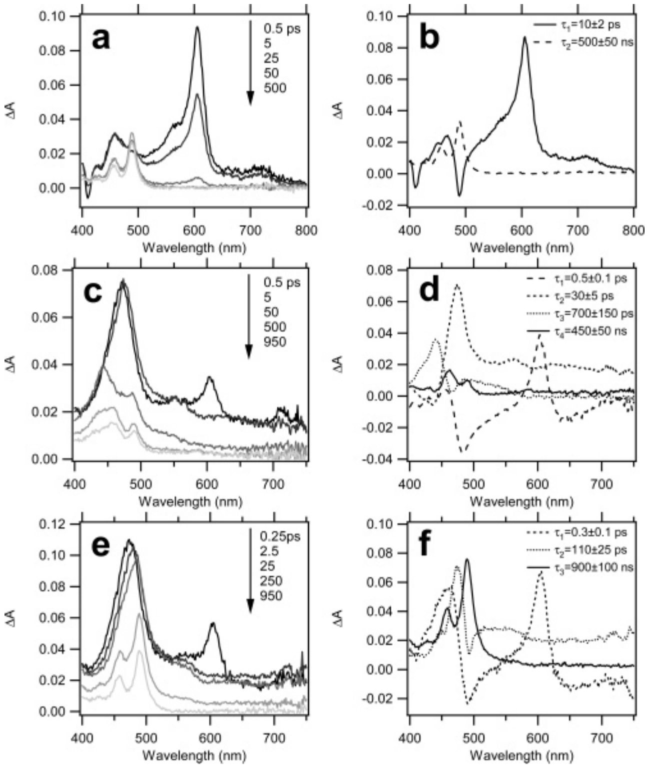
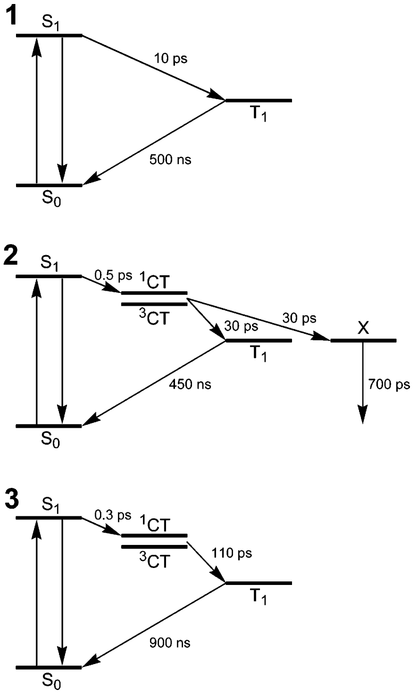


Figure 4. Time-resolved femtosecond transient absorption spectra (a, c, e) and decay-associated difference spectra (b, d, f) obtained by global analysis for **1**, **2**, and **3**, respectively. The lifetimes associated with the DADS are shown in b, d, and f as an inset. The longest components (>400 ns) are from the nanosecond transient absorption measurements.

The time-resolved spectra and DADS for compound **2** are given in Figure 4c,d. Compared with the spectra for compound **1**, the evolution of the spectra in time is different for **2**. Global analysis gives four different components with corresponding DADS. The component with a maximum at 603 nm and minimum at 481 nm in the DADS decays with a lifetime of 0.5 ps. The DADS of the second component has a maximum at 475 nm. This spectrum decays in 30 ps, and a new spectrum with two maxima at 442 and 486 nm appears simultaneously. The absorption band at 442 nm decays faster (700 ps) than that at 486 nm (≫1 ns). Although this spectrum looks similar to the triplet-state spectrum of **2** (vide supra), it does not match

SCHEME 1: Energy Level Diagrams Proposed for Excited-State Dynamics of 1, 2, and 3



exactly. This suggests that the spectrum at ~1 ns is a sum of the triplet-state absorption and the absorption of a transient with 700 ps lifetime.

The DADS (Figure 4d) with lifetime of 0.5 ps has a maximum (603 nm) at the same position as that of the singlet state of **1**. This suggests that this transient also arises from the singlet state. But for compound **2** the singlet state decays much faster and gives rise to a different spectrum than in the case of **1**. Apparently, the deactivation of the singlet state of **2** takes another route instead of direct ISC to the triplet state. The transient formed from the singlet state has an absorption maximum at 473 nm, and the absorption extends over the whole spectral range employed (up to 800 nm). We attribute this to the NDI radical anion, which is well described in literature from chemical, electrochemical, and photochemical reductions.[18,29] Normally this spectrum has a maximum around 470 nm and a weaker absorption band over 600 nm. The weaker absorption band is not clearly present in our data, which is likely due to the lower spectral resolution of the spectrograph and a lower signal-to-noise ratio of the setup employed. The appearance of the NDI radical anion would imply that the singlet state decays via a charge-transfer (CT) process, in which the phenyl moiety acts as electron donor to form a singlet CT state, in line with our previously mentioned hypothesis (vide supra).[37,38]

The CT state of NDI **2** has a lifetime of ~30 ps, and it decays simultaneously to the triplet state and to another unassigned state with a lifetime of 700 ps. However, in the nanosecond flash photolysis experiments only the triplet-state spectrum is observed. This means that the triplet state is formed via charge recombination from the CT state. The formation of the triplet requires a spin flip before it can reach the local triplet state (^{3}L). One possibility for this can be through ISC from ^{1}CT to ^{3}CT followed by charge recombination producing ^{3}L.[39] Another possibility is the direct transition from ^{1}CT to the local triplet state via spin−orbit coupling between the spin states of the ^{1}CT and the triplet manifold.[40] This mechanism has been proposed for other molecules with a large dihedral angle between the donor and the acceptor moieties.[41] A larger dihedral angle gives a significant change in the orbital angular momentum upon charge recombination. This requires a spin flip in order to conserve energy.[42] Since the dihedral angle between the phenyl ring and NDI is close to 90°, the direct transition from the ^{1}CT to a ^{3}L triplet state might also occur in this case. From our transient absorption data it is not possible to conclude which of the two mechanisms is prevalent in the present case, since the absorption spectra of the ^{1}CT and the ^{3}CT could be the same.

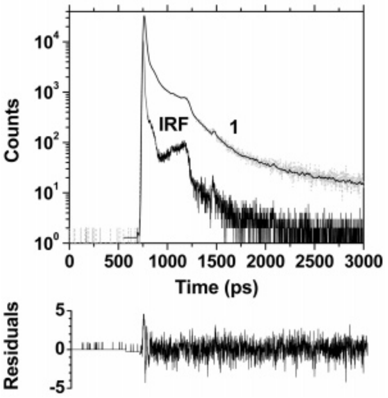


Figure 5. Representative picosecond fluorescence decay curve of **1** in chloroform at 410 nm with fitting residuals.

On this basis, a representative energy level diagram for **2** is given in Scheme 1. After excitation the singlet excited state decays via fast electron transfer to a ^{1}CT state. This state decays to the ^{3}L via either a ^{3}CT or a direct transition from ^{1}CT with simultaneous spin flip. From the ^{1}CT state also another species is formed, which has a maximum at 445 nm and a decay time of 700 ps. The presence of this species is clearly seen when the spectra at times 90 and 900 ps are compared (see Supporting Information). This is not observed with compound **3** (vide infra), which indicates that it might be caused by some intermediate formed during the decay process specific for **2**. Since we are mainly interested in the lifetimes of the excited singlet state of the molecules under study, detailed determinations of the nature of this intermediate fall outside the scope of this study.

The time-resolved spectra and DADS for the tetrahedral compound **3** are given in Figure 4e,f. Global analysis of the data for **3** shows three components. The first has a lifetime of 0.3 ps, and the DADS has maximum at 606 nm and minimum at 489 nm. The second DADS has a maximum at 476 nm and extends over the whole wavelength range. This species decays with a lifetime of 110 ps to the third spectrum, which shows maxima at 459 and 489 nm. The transients observed are similar to those of **2** except for the unassigned species, which suggest a similar decay pathway by rapid intramolecular electron transfer from the singlet state (0.3 ps). The formed ^{1}CT state decays with a lifetime of 110 ps to the triplet state, which has a lifetime of 900 ns as observed in the nanosecond transient absorption measurements. The energy level diagram for **3** is represented as given in Scheme 1.

The CT state of **2** has a higher energy than that of **3** (deduced from CT-fluorescence maxima), due to the driving force for charge recombination being larger for **2**. The lifetime of the CT state in **2** is shorter than that of **3**, which means that the rate of charge recombination is higher for a CT-state of higher energy (Marcus normal region).[43−45]

In summary, the femtosecond transient absorption measurements resulted in the observation of the singlet-state absorption and determination of the singlet-state dynamics (lifetime and decay routes) of a dialkyl-substitued NDI **1**. Substitution with

TABLE 1: Fluorescence Lifetimes and Relative Amplitudes (*A*) of the Components Obtained during the Analysis of the Decay Curves Observed at 410 nm

compd	*A* (%)	τ_1 (ps)	*A* (%)	τ_2 (ps)	*A* (%)	τ_3 (ps)	*A* (%)	τ_4 (ps)
1	89.5	12 ± 2	7.3	90 ± 20	1.7	500 ± 100	1.5	3000 ± 1000
2	96.2	1 ± 2	3.6	12 ± 2	0.1	300 ± 100	0.1	2000 ± 1000
3	81.7	3 ± 2	17.7	10 ± 2	0.4	300 ± 100	0.2	1000 ± 1000

a phenyl ring (**2** and **3**) on the imide nitrogen of NDI opens an additional decay pathway for the singlet state via intramolecular charge-transfer process.

Picosecond Fluorescence Lifetime Measurements. In order to support the singlet lifetimes observed in the femtosecond transient absorption, the corresponding fluorescence lifetimes were determined by time-correlated single-photon counting. The fluorescence decay traces following excitation with a 18 ps laser pulse ($\lambda_{exc} = 330$ nm) were monitored at 410 nm. A representative decay curve in chloroform is given in Figure 5. The concentrations of the solutions employed were on the order of 10^{-6} M. The data was fitted using iterative reconvolution of the instrument response function with a number of exponentials, generally with four exponentials. The obtained lifetimes are listed in Table 1.

For compound **1** the first component has a lifetime of ~12 ps, which is in agreement with the short component of 10 ps obtained from the femtosecond transient absorption data and confirms that it is from singlet state. Similar analysis on the decay curves obtained for **2** and **3** results in lifetimes of ~1 and ~3 ps, respectively, for the first components. These lifetimes are very short compared to the singlet lifetime of **1** (10 ± 2 ps). These short lifetimes are not very accurate since the instrumental response of the fluorescence lifetime measurements is ~18 ps (fwhm). Therefore we interpret these to be in agreement with the femtosecond absorption data obtained for **2** ($\tau = 0.5$ ps) and **3** ($\tau = 0.3$ ps), within the experimental errors. As the lifetime data from the femtosecond absorption data are more reliable on this time scale, those values should be taken as the lifetime of the respective singlet states. These short fluorescence lifetimes confirm that the excited singlet-state deactivation is much faster for compounds **2** and **3** than for **1**.

The fluorescence decays of all three compounds are multiexponentials. The origin of the components other than the shortest ones is not clear. Excimer formation by diffusion is highly unlikely in view of the short lifetimes observed for the singlet state. They might be attributed to excimer emission from ground-state aggregates. However, such ground-state aggregates were not visible in the steady-state absorption and are also not expected for the concentrations used (~10^{-6} M) during the single-photon counting experiments. If they are present at all, then it is only in very low quantities. These low quantities of aggregates could have a high luminescence quantum yield giving rise to the observed long components. Also triplet–triplet annihilation leading to delayed fluorescence could contribute to these long lifetimes. The complex nature of the fluorescence decay is not fully understood, and the details of this fall outside the scope of our present investigation.

TABLE 2: Fluorescence Maxima and Lifetimes of the CT Emission of 2 and 3 Observed at 545 and 530 nm, Respectively

	fluorescence maxima (nm)			fluorescence lifetime (ps)		
compd	CCl_4	$CHCl_3$	DCE	CCl_4	$CHCl_3$	DCE
2	540	559	570	25 ± 5	35 ± 10	50 ± 10
3	545	589	609	140 ± 30	170 ± 40	150 ± 30

The fluorescence decays of the CT-emission for compounds **2** and **3** were obtained by exciting with a 372 nm diode laser (fwhm of IRF ~87 ps) and detecting at 545 and 530 nm, respectively. The data was fitted using iterative reconvolution of the instrument response function with two exponentials. The second exponential had in all cases a lifetime of several nanoseconds and a relative amplitude less than one percent. The obtained fluorescence lifetimes of the CT emission bands of **2** and **3**, in three different solvents, are presented in Table 2. The lifetimes in chloroform qualitatively agree with the lifetimes obtained by the global analysis of the femtosecond transient absorption data. The lifetime of the CT state of compound **2** is shorter than that of **3** as observed in the femtosecond data. The fact that the CT-fluorescence lifetime matches with the lifetimes from transient absorption indicates that the CT state observed in the latter is from ^{1}CT. Since our kinetic data are in line with a direct transition from ^{1}CT into the ^{3}L, we suppose this is the decay route. However, the possibility of a two-step process with a very short-lived ^{3}CT state cannot be ruled out completely, because intersystem crossing from ^{1}CT to ^{3}CT may be followed by rapid charge recombination from the ^{3}CT to the local triplet, which would not show up in our experiments.

Fluorescence Lifetime Measurements at 77 K. The fluorescence decays in a low temperature (77 K) glass were also measured to further investigate the influence of the nitrogen substituents on the singlet-state deactivation. It is known that the ISC of alkyl-substituted NDIs hinges on the out-of-plane bending modes in carbonyl compounds, and it is thus slowed down in glasses.[29] This leads to less efficient triplet formation in rigid matrices, where the molecular motion is inhibited. For the phenyl substituents a different deactivation pathway is observed, and therefore it is expected that the rigid matrix does not affect the singlet deactivation process of compounds **2** and **3**. The fluorescence decays in a methyl-tetrahydrofuran (MTHF) glass at 77 K are depicted in Figure 6. The fluorescence lifetime of **1** in MTHF at 77 K becomes much longer (~1 ns) due to the slowing down of ISC process. For compounds **2** and **3** the fluorescence lifetimes remain short. This confirms that, in the case of NDIs substituted with a phenyl group on one of the nitrogen atoms, the singlet-state deactivation follows a different decay pathway, namely intramolecular electron transfer from the phenyl ring to the NDI moiety, as already inferred from the transient absorption experiments.

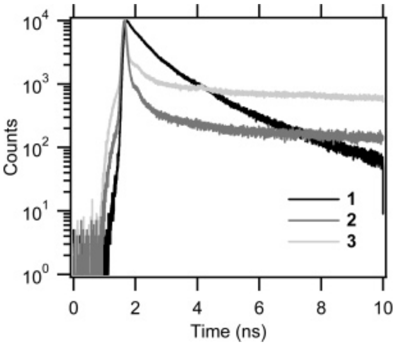


Figure 6. Fluorescence decay curves of **1**, **2**, and **3** in MTHF at 77 K.

Conclusions

NDI derivatives **1**, **2**, and **3** were studied with nanosecond to femtosecond time-resolved techniques. For the symmetrically substituted NDI **1** the excited singlet-state absorption (600 nm) and lifetime (10 ± 2 ps) are reported for the first time. The singlet state decays to ground state via efficient ISC. Substitution on imide nitrogen with a phenyl ring as in the case of **2** and **3** opens an additional decay pathway from the S_1 state to a local ^3L triplet state via an intramolecular charge transfer state (^1CT) resulting from electron transfer from the phenyl ring to the NDI moiety. As a consequence, the singlet-state lifetime is drastically reduced, which is in the range of ∼0.3−0.5 ps for **2** and **3**. This ^1CT state subsequently decays to the triplet state of NDI. The fluorescence lifetimes obtained are in close agreement with the lifetimes of the singlet state found with femtosecond transient absorption measurements. The difference in the singlet-state decays between **1** versus **2** and **3** was further proven by fluorescence lifetime measurements at 77 K in an MTHF glass. In MTHF glasses, the singlet-state lifetime remained short in the cases of **2** and **3**, but it increased to nanoseconds for **1** due to slowing down of the ISC process.

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Supporting Information Available: Transient absorption spectra of compound **2** in chloroform after 90 and 900 ps. This material is available free of charge via the Internet at http://pubs.acs.org.

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