

Chromophore Orientation-Dependent Photophysical Properties of Pyrene–Naphthalimide Compact Electron Donor–Acceptor Dyads: Electron Transfer and Intersystem Crossing

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charge transfer intersystem crossing (SOCT-ISC), we prepared naphthalimide (NI)-pyrene (Py) compact electron donor-acceptor dyads, in which pyrene acts as an electron donor and NI is an electron acceptor. The connection of the two units is at the 4-C and 3-C positions of the NI unit and the 1-position of the pyrene moiety for dyads NI-Py-1 and NI-Py-2, respectively. A charge transfer absorption band was observed for both dyads in the UV-vis absorption spectra. Upon nanosecond pulsed laser excitation, long-lived triplet states (lifetime is 220 μ s) were observed and the triplet state was confined to the pyrene moiety. The ISC efficiency is moderate to high in nonpolar to polar solvents (singlet oxygen



quantum yield: $\Phi_{\Delta} = 14-52\%$). Ultrafast charge separation (*ca*. 0.81 ps) and charge recombination-induced ISC (~3.0 ns) were observed by femtosecond transient absorption spectroscopy. Time-resolved electron paramagnetic resonance spectroscopy confirms the SOCT-ISC mechanism; interestingly, the observed electron spin polarization pattern of the triplet state is chromophore orientation-dependent; and the population rates of the triplet sublevels of **NI-Py-1** ($P_x:P_y:P_z = 0.2:0.8:0$) are drastically different from those of **NI-Py-2** ($P_x:P_y:P_z = 0:0:1$).

1. INTRODUCTION

To populate the triplet excited state of a chromophore is crucial in photochemistry, such as energy transfer and electron transfer processes and has attracted much attention in recent years. Strong absorption of light, high intersystem crossing (ISC) ability, and long-lived triplet excited states are the desired properties of efficient triplet photosensitizers (PSs). Triplet PSs are important for various applications such as photovoltaics,^{1,2} luminescence bioimaging,³ artificial photosynthesis,^{4,5} photodynamic therapy,^{6–9} and triplet-triplet annihilation photon up-conversion.^{10–13} The triplet excited state of organic compounds is populated by ISC. As the ISC is an electron spin forbidden process, different methods have been used to enhance the ISC ability in aromatic compounds. The most straightforward strategy is the utilization of heavy atoms (Br, I, Pt, Ir, etc.) based on the heavy atom effect-enhanced spin-orbit intersystem crossing (SO-ISC) mechanism.¹⁴⁻¹⁶ However, the presence of these atoms can shorten the triplet state lifetime and increase the cost of the material. Some other approaches have also been used to enhance the ISC in heavyatom free organic compounds, for instance, the $S_n \rightarrow T_m$ ($n \ge 1$ 1; $m \ge 1$) states energy matching,^{11,14} $n - \pi^* \leftrightarrow \pi - \pi^*$ transition (EI-Sayed rule),¹⁷ exciton coupling,¹⁸ electron spin convertor^{19,20} and charge recombination (CR)-induced ISC,²¹⁻²³ etc. However, all these methods exhibit some

disadvantages, for instance, the complicated synthesis or nonefficient ISC. Therefore, a simple method is highly desired in the design of heavy atom-free triplet PSs.

One promising approach to populate the triplet state without any heavy atom is the CR-induced ISC in electron donor-acceptor systems.^{21,24–26} Upon photoexcitation, charge separation (CS) occurs in electron donor-acceptor dyads and forms the charge transfer (CT) state, which can produce the triplet state (³LE, LE: locally excited) via the CR process or may decay to the ground state without ISC. Usually, the separation of the electron donor and acceptor in the conventional dyads is large, the electronic exchange energy is extremely small ($J < 0.01 \text{ cm}^{-1}$), and the purpose for preparation of those dyads is not to obtain a ³LE state, the long-lived ³CT state is usually populated by a radical-pair ISC (RP-ISC) mechanism.^{4,5,21} However, the large separation of the electron donor and acceptor makes the synthesis of the

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Scheme 1. Synthesis of the Compounds^a



"Key: (a) *n*-butylamine, EtOH, reflux at 78 °C for 5 h, under N_2 , yield: 62%; (b) pyrene-1-boronic acid, Pd(PPh₃)₂Cl₂, THF/H₂O, K₂CO₃, at 80 °C for 24 h, under N_2 , yield: 46%; (c) *n*-butylamine, EtOH, reflux at 80 °C for 6 h, under N_2 , yield: 60%; (d) similar to step (b), yield: 30%; (e) phenyl boronic acid, K₂CO₃, Pd(PPh₃)₄, EtoH/tol/H₂O (2:2:1 v/v/v), stirred at 70 °C for 9 h, under N_2 , yield: 56%; (f) and (g) similar to step (e), yields: 50 and 42%, respectively.

compounds difficult. Moreover, the RP-ISC is slow (a few ns), which makes the process ${}^{1}\text{CT} \rightarrow {}^{3}\text{CT} \rightarrow {}^{3}\text{LE}$ non-efficient. On the other hand, shortening the linker will increase the electronic coupling between the electron donor and acceptor, which leads to large electron exchange energy, and the RP-ISC is inhibited. Therefore, electron donor–acceptor dyads with more simple molecular structures are desired to attain efficient ISC.

Recently, CR-induced ISC was reported for the compact donor–acceptor dyads, in which electron donor and acceptor units are connected by a short linker and the two units adopt orthogonal geometry, and the mechanism is called spin-orbit charge transfer intersystem crossing (SOCT-ISC).^{24,27–30} In this mechanism, the CR is accompanied by a molecular orbital angular momentum change, which compensates the electron spin angular momentum change of ISC. As a result, the CRinduced ISC is enhanced in these compact orthogonal electron donor–acceptor dyads. Therefore, it is of particular interest for the preparation of heavy atom-free organic triplet photosensitizers with simplified molecular structures compared with other heavy atom-free triplet photosensitizers.^{22,27,31–34}

Until now, the reports related to SOCT-ISC are restricted to the chromophores of anthracene,^{27,35} bodipy,²⁴ naphthalenediimide (NDI),²⁸ and perylene.³⁶ Concerning the pyrene chromophore, it is rarely used for the preparation of dyads showing SOCT-ISC. However, to fully understand the SOCT-ISC efficiency as well as the electron spin selectivity of the ISC of these dyads, more examples are required. For instance, the spin dynamics of some systems are studied by time-resolved electron paramagnetic resonance (TREPR) spectroscopy.^{35,37,38} It was proposed that the electron spin polarization (ESP) pattern of the TREPR spectra of the triplet state accessed by SOCT-ISC is always different than the conventional SO-ISC mechanism.^{27,31,35} This is true but only for few cases: we found that the ESP pattern of the triplet TREPR spectra can be the same for both the mechanisms (SOCT-ISC and SO-ISC) and it is also dependent on the structures of electron donors/acceptors.^{30,36,38,39} Moreover, the effect of the mutual orientation of electron donor and acceptor chromophores on the SOCT-ISC efficiency and the electron spin selectivity was rarely studied.

Recently, we demonstrated that the perylene-naphthalimide compact dyad showed excellent ISC efficiency ($\Phi_{\Delta} = 80\%$) and the ISC mechanism was confirmed by TREPR spectroscopy.⁴⁰ We also found that the dyads with perylene as an electron acceptor also show efficient SOCT-ISC.³⁶ Previously, electron donor-acceptor dyads with bodipy as an electron acceptor and pyrene as an electron donor were reported to show moderate SOCT-ISC ($\Phi_{\Delta} = 25\%$ in EtOH; $\Phi_{\Delta} = 1\%$ in HEX).^{41–43} Inspired by these approaches, herein we designed new compact donor-acceptor dyads by using a pyrene $(\mathbf{P}\mathbf{y})$ moiety as an electron donor while naphthalimide (NI) acts as an electron acceptor, intending to tune the excited state properties, especially the electron spin selectivity of the ISC (Scheme 1). The conformation of the dyads is controlled by the hindered rotation around the linker (governed by steric hindrance) with different substitutional positions (3-C or 4-C positions of the NI moiety). The rotation around the linker can influence the electronic coupling or the kinetics of CS/CR and the ISC efficiency. We studied the photophysical properties of the dyads by using the steady-state and femtosecond/nanosecond time-resolved transient absorption spectroscopic methods as well as TREPR spectroscopy.

2. EXPERIMENTAL SECTION

2.1. General Procedures. All the chemicals and organic solvents used in the synthesis are analytically pure and were used as received. The solvents used in the anhydrous reactions were dried using molecular sieves. The UV/visible absorption spectra were taken on a UV-2550 dual-beam ultraviolet–visible spectrophotometer (Shimadzu Ltd., Japan). The fluorescence emission spectra were recorded on an RF-5301 PC spectrofluorometer (Shimadzu Ltd., Japan). Fluorescence lifetimes were measured on an OB920 luminescence lifetime

spectrometer (with TCSPC detection mode, Edinburgh Instruments Ltd., U.K.); the instrument response function (IRF) is 100 ps. For all the compounds, fluorescence lifetimes were measured with a 340 nm EPL picosecond pulsed laser (pulse width: 800 ps, maximum average power: 40 μ W). An Optistate DN cryostat (Oxford Instruments, U.K.) was used for low-temperature fluorescence spectra measurements.

2.2. Synthesis of NI-Py-1. Under a N₂ atmosphere, pyrene-1-boronic acid (139.4 mg, 0.56 mmol) and 4-bromo-1,8-naphthalic anhydride (143.9 mg, 0.43 mmol) were mixed in THF/H₂O (10 mL/1 mL). K₂CO₃ (596.6 mg, 4.3 mmol) was added, and the reaction mixture was bubbled with N₂ for 20 min. The catalyst $Pd(PPh_3)_2Cl_2$ (10 mg, 0.013 mmol) was added, and the mixture was stirred at 80 °C for 24 h. After cooling down, the product was extracted with DCM (3×20 mL), washed with water, and dried over anhydrous MgSO4. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (silica gel, DCM/PE = 1:3, v/v) to give a light yellowish solid (90 mg, yield: 46%). Mp: 194-196 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.82 (d, 1H, J = 8.0 Hz), 8.67 (d, 1H, J = 8.0 Hz), 8.36 (d, 1H, J = 8.0 Hz), 8.31 (d, 1H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.21 (d, 1H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.21 (d, 1H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.21 (d, 1H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.21 (d, 1H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.21 (d, 1H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.21 (d, 1H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.21 (d, 2H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.21 (d, 2H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.21 (d, 2H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.21 (d, 2H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.21 (d, 2H, J = 8.0 Hz), 8.22 (d, 3H, J = 8.0 Hz), 8.21 (d, 2H, J = 8.0 Hz), 8.21 (d, 3H, J =J = 8.0 Hz, 8.10-8.01 (m, 2H), 7.98-7.92 (m, 2H), 7.81 (d,1H, J = 8.0 Hz), 7.60–7.54 (m, 2H), 4.30 (t, 2H, J = 8.0 Hz), 1.87-1.79 (m, 2H), 1.59-1.49 (m, 2H), 1.06 (t, 3H, J = 8.0Hz). ¹³C NMR (CDCl₃, 125 MHz): δ 164.4, 164.2, 145.9, 133.4, 133.0, 131.5, 131.4, 131.3, 130.8, 130.7, 129.6, 129.4, 128.5, 128.2, 127.9, 127.3, 127.0, 126.4, 125.8, 125.5, 124.8, 124.7, 124.6, 124.5, 123.0, 122.4, 40.3, 30.3, 20.5, 13.9. TOF MS EI: Calcd ($[C_{38}H_{23}N]^+$), m/z = 453.1729; found, m/z =453.1718.

2.3. Synthesis of NI-Py-2. Compound NI-Py-2 was synthesized with a method similar to that of NI-Py-1. The product was obtained as yellow crystals (60 mg, yield: 30%). Mp: 132–134 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.94 (s, 1H), 8.70 (d, 1H, *J* = 8.0 Hz), 8.46 (s, 1H), 8.33 (d, 2H, *J* = 8.0 Hz), 8.29 (d, 1H, *J* = 8.0 Hz), 8.24 (d, 1H, *J* = 8.0 Hz), 8.18 (s, 2H), 8.14–8.06 (m, 4H), 7.86 (d, 1H, *J* = 8.0 Hz), 4.27 (t, 2H, *J* = 8.0 Hz), 1.84–1.76 (m, 2H), 1.56–1.49 (m, 2H), 1.03 (t, 3H, *J* = 8.0 Hz). ¹³C NMR (CDCl₃, 125 MHz): δ 164.2, 140.3, 135.4, 134.9, 133.9, 133.7, 131.9, 131.5, 131.3, 131.1, 130.9, 128.6, 128.3, 128.0, 127.7, 127.4, 127.3, 126.3, 125.6, 125.2, 125.0, 124.8, 124.4, 122.9, 122.8, 40.3, 30.3, 20.4, 13.9. TOF MS EI: Calcd ([C₃₆H₂₇N]⁺), *m/z* = 453.1729; found, *m/z* = 453.1720.

2.4. Polymer Film Preparation Method. The commercially available polyurethane precursors Clear Flex 50 (part A contains 4,4'-methylenedicyclohexyl diisocyanate and part B contains phenylmercury neodecanoate) and polymethyl methacrylate (PMMA), which are transparent at room temperature, were used to prepare the doped thin films of compounds. For Clear Flex 50 film preparation, part A and part B were mixed by weight (1:2 ratio) and stirred to a clear sticky mixture. To 150 μ L of Clear Flex 50 and 20 μ L of DCM was added the respective compound (20 μ L, $c = 2 \times 10^{-3}$ M in DCM) and mixed adequately. The mixed solution (100 μ L) was added dropwise onto the quartz plate (diameter is 17 mm, thickness is 1 mm), allowing the solvent to evaporate and the resulting film to dry for 24 h. For PMMA film preparation, PMMA (50 mg) was dissolved in THF (2 mL). Then, the respective compound (NI-Py-1 or NI-Py-2, etc. 20 μ L, *c* = 2 × 10^{-3} M) was added into PMMA solution (45 μ L) and mixed well. A total of 60 μ L of miscible liquids was taken to cast on

the quartz plate, with a similar method to that mentioned above. All the films were prepared before 24–36 h of measurements.

2.5. Electrochemical and Spectroelectrochemical Studies. The electrochemical measurements were carried out with a CHI610D electrochemical workstation (CHI instruments, Inc., Shanghai, China). In nitrogen-purged saturated DCM solution containing 0.10 M tetrabutylammonium hexafluorophosphate $(Bu_4N[PF_6])$ as a supporting electrolyte, the counter electrode was a platinum electrode, a glassy carbon electrode was the working electrode, and the Ag/AgNO₃ (0.1 M in ACN) couple was the reference electrode. A ferrocenium/ferrocene (Fc⁺/Fc) redox couple was used as an internal reference.

Spectroelectrochemistry measurements were performed using a 0.1 cm path length quartz electrochemical cell. The cell was equipped with a platinum gauze as the working electrode, a platinum wire as the counter electrode, and Ag/ AgNO₃ as the reference electrode. $Bu_4N[PF_6]$ was used as the supporting electrolyte. The potential was regulated with the CHI610D electrochemical workstation (CHI instruments, Inc., Shanghai, China), and the spectra were recorded using an Agilent 8453E UV-vis spectrophotometer (Agilent Technologies Inc., U.S.A.). Samples were deaerated with nitrogen for 5 min before measurement, and the nitrogen atmosphere was maintained during the measurements.

2.6. Femtosecond Transient Absorption Spectroscopy. The femtosecond experiments were performed using a Ti:sapphire laser system with ~100 fs pulse duration and 1 kHz repetition rate (Spectra Physics, Spitfire Pro XP) and a commercial ultrafast transient absorption spectrometer (Ultrafast System, Helios). The excitation wavelength was determined from the steady-state UV-vis absorption spectra and generated in an optical parametric amplifier (TOPAS, Light Conversion, U.S.A.). The magic angle between the probe and the pump beam polarization direction was used. The surface Xplorer and Glotaran software were used for processing the experimental data after chirp correction.⁴⁴

2.7. Nanosecond Transient Absorption Spectroscopy. The nanosecond transient absorption spectra were studied on a LP980 laser flash-photolysis spectrometer (Edinburgh Instruments Ltd., U.K.). The samples were purged with N_2 for 15 min before measurement and excited with a nanosecond pulsed laser (Opolette 355II + UV nanosecond pulsed laser, the wavelength is tunable in a range of 200–2200 nm. OPOTEK, U.S.A.). Typical laser power is 5 mJ per pulse. The signal was digitized with a Tektronix TDS 3012B oscilloscope, and the data was analyzed with L900 software.

2.8. Time-Resolved Electron Paramagnetic Resonance Spectroscopy. TREPR measurements were carried out at 80 K. The samples were excited at 355 nm (10 mJ pulse, 7 ns, 10 Hz) with a 400–900 ns time window. The measurements were done in frozen solution (*ca.* 10^{-3} M) and loaded in a quartz tube (1.6 mm o.d. × 1.1 mm i.d). A Bruker Elexsys E580 EPR spectrometer with a cylindrical resonator (EN 5107D2) at X-band (9.8 GHz) frequencies was used. The TR CW EPR spectra were obtained by the summation of the data in different time windows after the laser pulse. The EPR spectra were simulated using the EasySpin package implemented in the MATLAB programming language.⁴⁵

2.9. DFT Calculations. The geometries of the compounds were optimized using density functional theory with the

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B3LYP functional and 6-31G(d) basis set. There are no imaginary frequencies for all the optimized structures. The energy gaps between the S₀ state and the triplet excited states of the compounds were approximated based on the optimal ground state geometry. All these calculations were performed with Gaussian 09W software.⁴⁶

3. RESULTS AND DISCUSSION

3.1. Design Rationales of the NI–Pyrene Compact Electron Donor–Acceptor Dyads. To study the SOCT-ISC of compact electron donor–acceptor dyads, we build a bichromophoric system in which NI is used as an electron acceptor (Scheme 1). NI has extensively been used as a fluorophore due to its robust photophysical properties.^{47–49} On the other hand, the pyrene moiety is used as an electron donor.^{41,42} We synthesized NI-Py-1 and NI-Py-2 compact donor–acceptor dyads with different substitutional positions (Scheme 1). Previously, NI-Py-1 was reported with different alkyl chains, and basic photophysical properties were studied, i.e., UV–vis absorption and fluorescence properties, but the detailed ISC properties were not studied.⁵⁰

For NI-Py-1, the attachment of pyrenyl is made at the 4-C position of the NI moiety, and the geometry is expected to be orthogonal due to the steric hindrance. While for NI-Py-2, the connection is at the 3-C position of the NI unit, which gives a large degree of freedom for rotation due to the smaller steric hindrance imposed by the hydrogen atoms of pyrene and the NI moieties. The synthesis of the dyads was carried out with the Suzuki–Miyaura cross-coupling reactions. Py-Ph, NI-3Ph, and NI-4Ph were prepared as reference compounds (Scheme 1). The yields of the compounds were satisfactory, and the molecular structures were fully characterized by ¹H NMR, ¹³C NMR, HRMS spectroscopic methods.

3.2. UV–Vis Absorption and Fluorescence Emission Studies of Compounds. The UV–vis absorption spectra of the compounds are studied (Figure 1). The characteristic



Figure 1. UV–vis absorption spectra of the compounds (a) **Py**, **Py**-**Ph**, **NI-Py-1**, and **NI-Py-2** and (b) **NI-3Ph**, **NI-4Ph**, **NI-4Br**, and **NI**. $c = 1.0 \times 10^{-5}$ M, in dichloromethane. 20 °C.

absorption bands centered at 336 and 334 nm were observed for pristine pyrene and NI moieties, respectively, with significant vibrational progression. A slightly red-shifted absorption band was observed for **Py-Ph** with maxima at 345 nm, and the vibrational progression was lost. This result indicates strong electronic coupling between the phenyl and pyrene moieties. For **NI-Py-1**, the absorption is significantly red-shifted as compared with both pyrene and **NI**, showing strongly structured absorption bands, with the most intensive one at 343 nm (Figure 1a), which is characteristic absorption of the pyrene moiety.

Interestingly, for NI-Py-2, a broader LE absorption band was observed, which is different from NI-Py-1. For both the dyads at the red-end of the absorption spectra, a well-separated CT absorption band $(S_0 \rightarrow {}^1CT)$ in a range of 370–450 nm was observed (Figure 1a). This indicates that in both dyads, there is strong electronic interaction between the NI and the Py moieties at the ground state. For NI-3Ph and NI-4Ph, as a comparison with NI and NI-4Br, the absorption bands are also red-shifted to 338 and 347 nm, respectively (Figure 1b). This shows that the electronic coupling exists for NI-3Ph and NI-4Ph but weaker than that between NI and pyrene moieties in NI-Py-1 and NI-Py-2 dyads. Moreover, the weak absorption of the NI-Ph compounds may be attributed to the small transition dipole moments. From the charge-transfer absorption band in NI-Py-1 and NI-Py-2 dyads, the electronic coupling matrix element (V_{DA}) between the S₀ and Frank Condon S₁ state was calculated by using eq 1

$$V_{\rm DA}(\rm cm^{-1}) = \left(\frac{2.06 \times 10^{-2}}{R}\right) (\varepsilon_{\rm max}^{\rm CT} \nu_{\rm max}^{-\rm CT} \Delta \nu_{1/2}^{-\rm CT})^{1/2}$$
(1)

where *R* is the separation between the center of an electron donor and acceptor, in Å; $\varepsilon_{\rm max}^{\rm CT}$ is the molar absorption coefficient at the maximum of the CT absorption band, in $[M^{-1} \ {\rm cm}^{-1}]$; $\nu_{\rm max}^{-{\rm CT}}$ is the absorption maximum of the CT absorption band in a wavenumber scale, in cm⁻¹; and $\Delta \nu_{1/2}^{-{\rm CT}}$ is the full width of the band at the half-maximum, in cm⁻¹. The distance between the center of the donor and acceptor is determined by DFT optimization. Herein, $R_{\rm NI-Py-1} = 7.31$ Å and $R_{\rm NI-Py-2} = 7.68$ Å are used to calculate the $V_{\rm DA}$. The CT absorption bands were isolated by simulation with origin software.

The V_{DA} values of NI-Py-1 and NI-Py-2 were calculated as 0.17 and 0.087 eV, respectively. The V_{DA} of NI-Py-2 is smaller than that of NI-Py-1 because the orientation of the acceptor moiety to the 3-C position slightly increases the separation between the center of the electron donor and acceptor in NI-Py-2.

The fluorescence properties of the compounds were studied (Figure 2). Pristine Py and NI show characteristic emission profiles with fluorescence maxima at 372 and 378 nm, respectively, with a significant vibrational progression. Similarly, fluorescence for Py-Ph was observed at 380 nm; under the same experimental conditions, however, the intensity of the emission band is higher than that of pristine pyrene (Figure 2a). The fluorescence quantum yields of Py and Py-Ph are 8 and 13%, respectively (Table 1). The fluorescence of NI-3Ph and NI-4Ph was observed at 414 and 420 nm, respectively. The fluorescence quantum yields were determined as 31 and 51%, respectively (Table 1).

For NI-Py-1, the locally excited (LE) state emissions of Py and NI moieties are completely quenched and a broad, structureless emission band centered at 538 nm was observed (Figure 2a), which is assigned to CT emission. For NI-Py-2, the LE fluorescence is also significantly quenched while a minor emission band at 384 nm and a more intense broad band at 550 nm were observed (Figure 2a). The emission band at higher energy is assigned as the residual LE state emission of the pyrene moiety, whereas the band at lower energy is attributed to CT emission. In both dyads, the fluorescence of the NI moiety is also quenched. The most probable reason, for the quenched fluorescence, is the photo-induced charge



Figure 2. (a) Fluorescence emission spectra of the compounds ($\lambda_{ex} = 325 \text{ nm}$, A = 0.26). Optically matched solutions were used in DCM, c = ca. 1.0 × 10⁻⁵ M. Fluorescence emission spectra of compounds in different solvents: (b) NI-Py-1 ($\lambda_{ex} = 325 \text{ nm}$) and (c) NI-Py-2 ($\lambda_{ex} = 325 \text{ nm}$). Optically matched solutions were used ($c \approx 1.0 \times 10^{-5} \text{ M}$, A = 0.26). 20 °C.

Table 1.	Photophy	vsical Paramete	ers of the	Compounds ⁴
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compounds	$\lambda_{\rm abs}$ [nm]	ε^{b}	$\lambda_{\rm F}^{\ c} [\rm nm]$	$\Phi_{\scriptscriptstyle \mathrm{F}}^{}d}$ [%]	$\tau_{\rm F}^{e}$ [ns]	$k_{\rm r}^{f} [10^5 {\rm s}^{-1}]$	$k_{\rm nr}^{\ g} \ [10^6 \ {\rm s}^{-1}]$	$\tau_{\rm T}^{\ h} \ [\mu s]$
Ру	336	4.56	372	8	7.9 ⁱ	1.50	2.35	146.2
Py-Ph	345	3.06	380	13	7.8^{i}	3.09	2.07	202 ¹
NI	334	1.72	378	1.5	0.24	6.25	41.0	79.2 ^j
NI-3Ph	338	0.99	414	31	3.4	9.11	2.02	358 ¹
NI-4Ph	347	1.67	420	51	3.5	14.16	1.36	332 ¹
NI-Py-1	343/400	5.08/0.76	538	78, ⁱ 73, ^j 36, 20 ^k	4.4	8.18	1.45	215 ¹
NI-Py-2	347/400	4.51/0.50	550	62, ⁱ 50, ^j 14, 7 ^k	6.0	2.33	1.43	220 ¹

^{*a*}In DCM (1.0 × 10⁻⁵ M). ^{*b*}Molar absorption coefficient: 10⁴ M⁻¹ cm⁻¹. ^{*c*}Fluorescence maxima. ^{*d*}Absolute luminescence quantum yield measured by an optical integrated sphere. Py and Py-Ph ($\lambda_{ex} = 330$ nm) and NI-3Ph, NI-4Ph, NI-Py-1, and NI-Py-2 ($\lambda_{ex} = 340$ nm). ^{*c*}Fluorescence lifetime. Note that the IRF of a fluorescence lifetime spectrometer is *ca*. 100 ps. ^{*f*}Radiative decay rate constant $k_r = \Phi/\tau$. ^{*b*}Nonradiative decay rate constant $k_{nr} = (1 - \Phi)/\tau$. ^{*h*}Triplet state lifetime monitored by nanosecond transient absorption spectroscopy. ^{*i*}In *n*-hexane. ^{*j*}In toluene. ^{*k*}In ACN. ^{*l*}Intrinsic triplet excited state lifetime obtained by fitting the experimental curves with a TTA-based kinetic model.^{38,54}

transfer from the pyrene unit to the NI unit to form a ${}^{1}\text{CT}$ state.

The solvent polarity-dependent fluorescence of the compounds was studied (Figure 2b,c). For both the dyads, the fluorescence is highly dependent on solvent polarity, which is red-shifted, and the emission intensity decreased from nonpolar solvents to moderate polar solvents and further quenched in polar solvents; these are the typical CT emission features. This trend is in line with fluorescence quantum yields of the dyads in solvents with different polarity (i.e., for NI-Py-1, $\Phi_F = 78\%$ in *n*-hexane, 36% in DCM, and 20% in ACN). Note that the emission bands of the two dyads in HEX are broad and structureless and they are also CT features. Thus, we conclude that the emissive singlet states of the dyads are in substantial ¹CT features. The weak emission of NI-Py-1 and NI-Py-2 is attributed to the ISC from the ¹CT state (see the later section).

To study the energy and electron transfer process in the dyads, the fluorescence excitation (monitored at the CT emission band) and UV-vis absorption spectra are compared (Figure 3). The excitation spectra in a range of 370-450 nm are normalized with the UV-vis absorption, and the slightly lower magnitude in the LE absorption region shows that other nonradiative decay channel exists upon photoexcitation into the LE absorption bands, such as ISC of **NI** or the pyrenyl moiety.

It is known that **NI** has ISC ability due to the $\pi - \pi^* \rightarrow$ n $-\pi^*$ transition (S₁ \rightarrow T₄ energy level matching).⁵¹ For the reference compounds, **NI-3Ph** and **NI-4Ph**, the fluorescence is intensified with increasing the solvent polarity (Figure S17); this implies that in solvents with different polarity, the order of



Figure 3. Normalized fluorescence excitation (marked as Ex.) and UV–vis absorption spectra (in $1 - 10^{-A}$) of (a) **NI-Py-1** ($\lambda_{em} = 540$ nm) and (b) **NI-Py-2** ($\lambda_{em} = 545$ nm). In DCM. $c = 1.0 \times 10^{-5}$ M. 20 °C.

the energy of the $n-\pi^*$ and $\pi-\pi^*$ states may be changed, and thus the fluorescence becomes stronger in polar solvents, in which the $\pi-\pi^*$ state is slightly lower than the $n-\pi^{*,52}$ Similarly, both pyrene and **Py-Ph** have the ISC ability upon photoexcitation. The solvent polarity effect on fluorescence was studied (Figure S17), and similar results were observed. Thus, nonradiative decays are more efficient in nonpolar solvents for these compounds.

The phosphorescence emission spectra of dyads at 77 K in THF were studied (Figure S18). Upon addition of 20% iodoethane, the dyads showed a weak phosphorescence peak in the range from 510 to 650 nm. The phosphorescence lifetime of **NI-Py-2** is determined as 6.5 μ s in the frozen THF matrix, which is slightly shorter than the previously reported phosphorescence lifetime of the pyrene moiety (~9.4 μ s).¹⁷



Figure 4. Fluorescence lifetime decay traces of the dyads: (a) **NI-Py-1** at 480 nm (in toluene), at 538 nm (in DCM), and at 582 nm (in ACN), (b) **NI-Py-2** at 483 nm (in toluene), at 546 nm (in DCM), and at 592 nm (in ACN), (c) **NI-Py-2** at the 384 nm LE emission band in different solvents. The solvents used in the measurements are indicated. Excited with a picosecond pulsed laser (340 nm). $c = 1.0 \times 10^{-5}$ M. 20 °C.



Figure 5. Temperature-dependent fluorescence spectra of (a) NI-Py-1 and (b) NI-Py-2 in deaerated DCM. (c) Corresponding decay curves of NI-Py-2 at the 384 nm LE band (inset: fluorescence decay trace of the CT emission band at 550 nm). $c = 1.0 \times 10^{-5}$ M. $\lambda_{ex} = 340$ nm.

Similar results were observed for the NI-Py-1 dyad. Moreover, in a previous study, the phosphorescence spectrum of the NI-Py analogue dyad was observed almost in the same spectral region.⁵⁰

The fluorescence lifetimes of the dyads were studied by using a time-correlated single-photon counting (TCSPC) detection technique (Figure 4). The luminescence lifetime of **NI-Py-1** monitored at the CT emission band in toluene is 3.8 ns (Figure 4a), and interestingly, the fluorescence lifetimes are 4.4 and 6.0 ns in DCM and ACN solvents, respectively (with mono-exponential features). These extended fluorescence lifetimes in polar solvents are reasonable because the ${}^{1}\text{CT} \rightarrow S_{0}$ transition is actually a forbidden transition (weakly allowed), and thus the fluorescence lifetime can become longer.

Meanwhile, in the case of NI-Py-2 (Figure 4b), the luminescence lifetimes slightly decreased with increasing the solvent polarity, and the mono-exponential decay was observed with lifetimes of 8.1, 6.0, and 5.0 ns in toluene, DCM, and ACN, respectively. For NI-Py-2, the fluorescence lifetime at the LE emission band is also measured (Figure 4c), and an extended fluorescence lifetime was observed (τ_{LE} = 10.9 ns, in DCM) as compared with CT emission ($\tau_{\rm CT}$ = 6.0 ns, in DCM). For NI-Py-2, the fluorescence lifetime is slightly shortened in polar solvents, with the trend being opposite to that of NI-Py-1. As the ${}^{1}CT \rightarrow S_{0}$ transition is weakly allowed, thus the CT fluorescence lifetime can become longer than the LE emission. However, the longer emission wavelength (which can reduce the ${}^{1}CT/S_{0}$ energy gap) makes the nonradiative transition more significant, which may shorten the fluorescence lifetime for the ¹CT state. That could be the reason for shortening of the fluorescence lifetimes of NI-Py-2. These results are in agreement with the red-shifting of CT emission bands of the dyads. For instance, NI-Py-1 shows CT bands at 538 and 577 nm in DCM and ACN, respectively. Meanwhile, in NI-Py-2, the CT emission bands are more red-shifted and

appear at 550 nm (in DCM) and 590 nm (in ACN). The fluorescence lifetimes of pyrene, **Py-Ph**, pristine **NI**, and NI-Ph derivatives are also measured (Figure S19).

To further study the properties of CT emission features of the dyads, the temperature-dependent fluorescence spectra were studied in DCM (Figure 5). For both dyads, the fluorescence intensity was decreased and red-shifted at lower temperature, which is anomalous.⁵³ For NI-Py-2, with decreasing the temperature from 297 to 197 K, the CT band fluorescence intensity is significantly reduced, while the LE band at 384 nm is almost the same (Figure 5b). Similarly, for NI-Py-1, the CT emission band is reduced as temperature decreases (Figure 5a) but with less extent as compared with NI-Py-2. These results are anomalous but can be rationalized by the twisted intramolecular charge transfer emissive S₁ state.52 With decreased temperature, the thermal energy also decreased and the mutual orientation of the two moieties adopted more orthogonal conformation (energy minimized). Therefore, the intensity of the CT emission band is reduced because the radiative transition of ${}^{1}CT \rightarrow S_{0}$ is forbidden. As the geometry approaches orthogonal, the CT emission band will be red-shifted due to the lower energy of the CT state showing orthogonal geometry.⁵²

The effect of temperature on fluorescence lifetimes was also studied (Figure 5c and Figure S20). For NI-Py-2, at the LE emission band with decreasing temperature, the fluorescence lifetime is slightly increased with a biexponential decay feature, for instance, at 297 K ($\tau_1 = 0.19$ ns, 53% and $\tau_2 = 13.8$ ns, 47%) to ($\tau_1 = 0.68$ ns, 11% and $\tau_2 = 16.2$ ns, 89%) at 197 K. Interestingly, for the CT emission band, the fluorescence lifetime is also prolonged but with a mono-exponential decay feature (6.4 ns, at 297 K) with lowering the temperature (9.1 ns, at 197 K). Similar results were observed for NI-Py-1 when the temperature decreased from 297 K ($\tau_F = 4.4$ ns) to 157 K ($\tau_F = 9.0$ ns) (Figure S20).

The singlet oxygen quantum yields (Φ_{Δ}) of the compounds were studied (Table 2). For reference compounds NI-3Ph, NI-

Table 2. Singlet Oxygen Quantum Yields (Φ_{Δ}) of the Compounds in Different Solvents^{*a*}

compounds	HEX (31.0)	TOL (33.9)	DCM (40.7)	ACN (45.6)
Ру	30	34	26	35
Py-Ph	49	46	38	38
Py-Br	33	40	45	32
NI	13	15	34	46
NI-3Ph	65	38	30	22
NI-4Ph ^b	72	36	25	21
NI-3Br	15	40	53	54
NI-4Br ^c	25	36	64	64
NI-Py-1	17	14	32	52
NI-Py-2	26	20	36	47

^aSinglet oxygen quantum yield (Φ_{Δ}) with anthracene as the standard ($\Phi_{\Delta} = 0.70$ in MeOH) in different solvents. The values in the parentheses are the $E_{\rm T}$ (30) values of the solvents, in kcal mol⁻¹. ^bLiterature values.⁵⁵

4Ph, and Py-Ph, the singlet oxygen quantum yield is higher in nonpolar solvents ($\Phi_{\Delta} = 65$, 72, and 49% in *n*-hexane, respectively). However, the Φ_{Δ} values are decreased with increasing the solvent polarity, while Py-Ph shows a relatively solvent polarity-independent singlet oxygen production. In polar solvents, for instance, in ACN, Py and NI show moderate Φ_{Δ} values of 35 and 46%, respectively. For NI-Py-1 and NI-Py-2 dyads, the Φ_{Δ} is dependent on solvent polarity, and in nonpolar solvents, the Φ_{Δ} is lower (14–20%). Meanwhile, in medium polarity solvents such as DCM, the Φ_{Δ} values are 32 and 36% for NI-Py-1 and NI-Py-2, respectively.

Interestingly, the Φ_{Δ} is increased further in solvents with higher polarity; for instance, in ACN, Φ_{Δ} values of 52 and 47% were observed for NI-Py-1 and NI-Py-2, respectively (Table 2). This observation is different from the previously reported dyads, where most of the compounds showed negligible Φ_{Δ} in both nonpolar and polar solvents. Interestingly, the current dyads (NI-Py-1 and NI-Py-2) showed the highest Φ_{Δ} in polar solvents. We attribute this solvent polarity-dependent ${}^{1}O_{2}$ sensitizing behavior of the dyads to the different energy level matching of ${}^{1}CT$ and triplet states in different solvents. This strong solvent polarity dependency of the Φ_{Δ} value is an indication of the SOCT-ISC mechanism.

3.3. Electrochemical Study. The electrochemical properties of the compounds were studied by cyclic voltammetry (Figure 6 and Table 3). Pyrene and **Py-Ph** show a reversible oxidation wave at +0.75 and +0.77 V (vs Fc/Fc^+), respectively, and no reduction wave was observed (Figure 6a and Table 3). For NI-3Ph and NI-4Ph, a quasi-reversible reduction wave was observed at -1.82 and -1.84 V (vs Fc/Fc⁺), respectively, and no oxidation wave was observed (Figure 6a). For NI-Py-1, a reversible oxidation wave at +0.78 V and a quasi-reversible reduction wave at -1.84 V were observed (Figure 6b). Similarly, for NI-Py-2, a reversible oxidation wave at +0.78 V and a quasi-reversible reduction wave at -1.80 V were observed (Figure 6b), which are assigned to the oxidation of the pyrene moiety and the reduction of the NI moiety, respectively. The similar oxidation potentials of the dyads NI-Py-1 and NI-Py-2 (ca. +0.78 V) and Py-Ph (+0.75 V) and the similar reduction potentials of the dyads (ca. -1.8 V, vs Fc/ Fc^+) and NI-3Ph and NI-4Ph (*ca.* -1.8 V, vs Fc/Fc^+) indicate



Figure 6. Cyclic voltammogram of (a) reference **Py-Ph** and **NI-3Ph** and (b) dyads **NI-Py-1** and **NI-Py-2**. Ferrocene (Fc) was used as an internal reference (set as 0 V in the cyclic voltammograms). Scan rates: 50 mV/s. $c = 1.0 \times 10^{-3}$ M. UV–vis absorption spectral changes of **NI-Py-1** measured with the spectroelectrochemical method: (c) upon oxidation under 1.17 V and (d) upon reduction under -1.70 V. All the experiments were carried out in deaerated DCM containing Bu₄N[PF₆] (*ca.* 0.1 M) as supporting electrolytes and Ag/AgNO₃ as the reference electrode. 20 °C.

Table 3. Electrochemical Redox Potentials of the Compounds a

compounds	$E_{\rm OX}$ (V)	$E_{\rm RED}$ (V)
	-0x ()	-RED ()
NI-Py-1	+0.78	-1.84
NI-Py-2	+0.78	-1.80
Ру	+0.75	Ь
Py-Ph	+0.77	Ь
NI-3Ph	b	-1.82
NI-4Ph	b	-1.84

^{*a*}Cyclic voltammetry in N₂-saturated DCM containing 0.10 M Bu_4NPF_6 . The counter electrode is a Pt electrode, the working electrode is a glassy carbon electrode, ferrocene (Fc/Fc⁺) is the internal reference, and Ag/AgNO₃ couple is the reference electrode. ^{*b*}Not observed.

negligible interaction between the NI and Py units in the dyads at ground states (S_0). Thus, for both the dyads upon photoexcitation, the pyrene unit will act as an electron donor and the NI unit as an electron acceptor. Compared with the previously reported perylene-NI dyad,⁴⁰ the reduction potential of the NI moiety is similar (-1.83 V). The oxidation potential of the pyrene moiety of NI-Py-1 and NI-Py-2 is +0.78 V, as compared with the perylene-NI dyad (+0.55 V), indicating that the pyrene moiety is a weaker electron donor compared to the perylene moiety.

Furthermore, spectroelectrochemistry was also measured to study pyrene radical cation and **NI** radical anion absorption in NI-Py dyads. By applying a positive potential (1.17 eV, vs Ag/ AgNO₃) to **NI-Py-1**, we observed the generation of absorption bands centered at 355, 492, 600, and 656 nm (Figure 6c). It is almost similar to that observed for **Py-Ph** under similar experimental conditions (Figure S21a). Thus, these bands are assigned to the pyrenyl radical cation absorption. When a negative potential (-1.70 eV, vs Ag/AgNO₃) was applied, -0.01

-0.01

NI-Py-1⁶

NI-Py-2^b

3.61

3.62

2.16

2.12

2.40

2.37

Dyads in Differen	nt Solvents							
$\Delta G^0_{ m \ CS}$ (eV)				$E_{\rm CSS}$	(eV)			
compounds	HEY	TOI	DCM	ACN	HEY	TOI	DCM	ACN

-1.23

-1.26

Table 4. Driving Forces of Charge Separation (ΔG^0_{CS}) and the Energy Levels the of Charge Separated State (E_{CSS}) of the

 ${}^{a}E_{00} = 3.63 \text{ eV}$. ${}^{b}E_{00} = 3.63 \text{ eV}$. E_{00} is the approximated energy level based on the crossing point of UV-vis absorption and fluorescence emission after being normalized at the absorption/emission bands of the pyrene moiety.

-1.47

-1.50

absorption bands at 428, 502, 698, and 780 nm were observed (Figure 6d) for NI-Py-1. This result is in agreement with that observed for NI-4Ph (Figure S21b), and therefore, we can assign these bands to NI radical anion absorption. Similar results were observed for the NI-Py-2 dyad (Figure S21c,d). All these results are in agreement with the previous observations, 56,57 and the data are helpful for study of the charge separated state in femtosecond transient absorption spectra (see Section 3.5).

-0.33

-0.34

The Weller equations (see eqs S2 and S3 in the Supporting Information) were used to determine the charge separation state (CSS) and the driving force of intramolecular charge separation (Gibbs free energy changes of the photo-induced electron transfer process, $\Delta G_{\rm CS}$), and the results are summarized in Table 4; further details are given in the Supporting Information. The $\Delta G_{\rm CS}$ values indicated that the charge separation is thermodynamically allowed even in nonpolar solvents for both the dyads, for instance, in Hex ($\Delta G_{\rm CS} = -0.01 \text{ eV}$) and in toluene ($\Delta G_{\rm CS} = -0.33 \text{ eV}$) for NI-Py-1. The $\Delta G_{\rm CS}$ values are more negative in polar solvents, and a similar trend of $\Delta G_{\rm CS}$ values is observed for NI-Py-2. These results are in agreement with the experimental observations.

3.4. Nanosecond Transient Absorption (ns-TA) Spectroscopy: Triplet Excited States Properties of the **Compounds.** Nanosecond transient absorption (ns-TA) spectra were measured to study the triplet state production of the compounds (Figure 7). For NI-Py-1 upon nanosecond pulsed laser excitation, a negative peak centered at 340 nm was observed, which is in agreement with the UV-vis absorption spectra, and thus it is assigned as the ground state bleach (GSB) band. Moreover, a broad excited state absorption (ESA) band in a range of 400-840 nm was observed (Figure 7a). The apparent triplet state lifetime of NI-Py-1 is 105.8 μ s $(c = 2.0 \times 10^{-5} \text{ M}, \text{ in deaerated DCM})$. Moreover, the transient species lifetime of NI-Py-1 is significantly reduced under aerated conditions (0.68 μ s), which confirms the formation of triplet species. The intrinsic triplet state lifetime of the transient species of NI-Py-1 was determined as 215 μ s by monitoring the decay trace at 460 nm (Figure 7b) and by fitting the decay traces with a kinetic model with the triplettriplet annihilation quenching effect considered (complete details of TTA-based triplet lifetime fitting are given in the Supporting Information).^{30,38,54}

It should be noted that for the compounds showing high ISC yields and long triplet state lifetimes, the reported lifetimes are shorter than the intrinsic triplet state lifetime. The TTA self-quenching effect can significantly reduce the lifetime, and therefore it is important to get the real triplet state lifetimes. The triplet state in **NI-Py-1** is mainly localized on the pyrene moiety $(T_1 \rightarrow T_n)$ transition of the **Py** moiety), supported by TREPR and triplet spin density distribution (see the next sections).



3.29

3.30

Figure 7. Nanosecond transient absorption spectra of (a) **NI-Py-1** and (b) the decay trace at 460 nm. (c) Transient absorption spectra of **NI-Py-2** and (d) the decay trace at 470 nm. $\lambda_{ex} = 355$ nm. $c = 2.0 \times 10^{-5}$ M in deaerated DCM. 20 °C. Note: the triplet lifetimes are intrinsic triplet state lifetimes obtained by fitting the decay traces with a TTA-based kinetic model.^{38,54}

For NI-Py-2, a different transient profile was observed upon laser excitation as compared with NI-Py-1, except the GSB band centered at 345 nm (Figure 7c). A broad ESA band was observed in a range of 400-600 nm, although this ESA band is different than NI-Py-1, but it is similar to the ESA band of Py-Ph (Figure 8e). In DCM, the intrinsic triplet state lifetime of NI-Py-2 was determined as 220 μ s (Figure 7d), which is much longer than the apparent triplet lifetime, $\tau = 84.8 \ \mu s$. For these dyads, we propose that the triplet state is most probably localized on the pyrene moiety because the ³pyrene state is lower (2.10 eV) than the ³NI state (2.21 eV).^{47,58} This is also demonstrated by the presence of the significant GSB band (note that the NI moiety in the dyads gives much weaker absorption than the pyrene moiety) (Figure 1). This assignment is further supported by the TREPR spectral study (see the later section). The ns-TA spectra of NI-Py dyads were also studied in HEX and ACN (Figures S22 and \$23). The pyrene-localized triplet state was observed with almost similar transient features to those observed in the DCM solvent. However, the triplet state lifetimes are short in HEX (τ = 29.5 μ s) and long in ACN (τ = 300.4 μ s).

For reference compounds **NI-3Ph** and **NI-4Ph**, the ISC is efficient in nonpolar solvents and it varies with solvent polarity. It is known that for the unsubstituted **NI** moiety, the ISC is due to the $S_1 \rightarrow T_4$, a $\pi - \pi^* \rightarrow n - \pi^*$ transition.⁵¹ The $n - \pi^*$ state energy is more sensitive to the solvent polarity than the



Figure 8. Nanosecond transient absorption spectra of (a) **NI-3Ph**, in deaerated toluene ($c = 2.0 \times 10^{-5}$ M), and (b) the decay trace at 475 nm. (c) Nanosecond transient absorption spectra of **NI-4Ph**, in deaerated toluene ($c = 2.0 \times 10^{-5}$ M), and (d) the decay trace at 540 nm. (e) Nanosecond transient absorption spectra of **Py-Ph**, in deaerated *n*-hexane ($c = 1.0 \times 10^{-5}$ M), and (f) the decay trace at 450 nm, $\lambda_{ex} = 355$ nm. 20 °C. τ_{int} is the intrinsic triplet state lifetimes obtained by fitting of the data with a TTA-based kinetic model.^{38,54}



Figure 9. Femtosecond transient absorption spectra of (a) NI-Py-1 at different delay time, (b) respective evolution-associated difference spectra (EADS) obtained after global fitting, and (c) decay traces at selected wavelengths. In DCM. λ_{ex} = 350 nm. 20 °C.

 $\pi-\pi^*$ state, and thus the ISC efficiency of NI-3Ph and NI-4Ph could be solvent polarity-dependent as shown previously.⁴⁰ Similarly, the ISC of the pyrene moiety is known for a long time, and the ISC is due to the $S_n \rightarrow T_m$ energy matching.⁵⁹

The nanosecond transient absorption spectra of NI-3Ph, NI-4Ph, and Py-Ph were studied (Figure 8). For NI-3Ph, an ESA band in a range of 370-670 nm was observed, which is the typical feature of the NI triplet state absorption.⁶⁰ A minor GSB band is present at 350 nm, and the intrinsic triplet state lifetime was determined as 358 μ s in toluene (Figure 8a,b). Similarly, the nanosecond transient absorption spectra of NI-4Ph were studied, with an intrinsic triplet state lifetime of 332 μ s (Figure 8c,d). The NI localized triplet ESA band in a range of 370-670 nm was observed, similar to that we reported previously.⁴⁰ On the other hand, for **Py-Ph**, a strong GSB band observed at 340 nm and an ESA band in a range of 370-550 nm were detected upon laser excitation (Figure 8e). The intrinsic triplet state lifetime was determined as 202 μ s (Figure 8f), which is longer than the apparent triplet state lifetime (τ = 82 μ s). It is important to notice that the observed ESA band of Py-Ph is comparable with the ESA band of NI-Py-2. Furthermore, the strong GSB bands in dyads match well with the GSB bands of Py-Ph, while for NI-3Ph, the GSB band is very weak and the GSB band of NI-4Ph is also weaker. This observation further supported that the triplet state is localized

on the pyrene moiety in the dyads. Although for NI-Py-1, the triplet state ESA is rather different and broad in a range of 400–840 nm, as the substitution at 4-C of the NI moiety, which makes different electronic coupling in NI-Py-1. For pyrene upon photoexcitation, a broad ESA band in a range of 360-550 nm was observed upon the addition of 30% iodoethane. The lifetime of transient species was determined as 146.2 μ s (Figure S24).

The triplet excited state lifetimes of the compounds were also determined in polymer films, prepared by doping the compounds with the polymethylmethacrylate (PMMA) matrix and commercially available transparent polyurethane rubber (Clear Flex 50) (Figure S26). Interestingly, in both the media, the triplet state lifetimes of the compounds were extended up to the millisecond timescale as compared to that in the deaerated solution. **NI-Py-1** exhibited triplet lifetimes of 25.4 ms (in PMMA) and 24.8 ms (in Clear Flex 50); similarly, for **NI-Py-2**, triplet state lifetimes were determined as 27.5 and 24 ms, respectively (in doped PMMA and Clear Flex 50 thin films under a N₂ atmosphere). Similarly, extended triplet state lifetimes were also observed for reference compounds (Figure S27).

3.5. Femtosecond Transient Absorption (fs-TA) Spectroscopy. In order to investigate charge separation, charge recombination, and intersystem crossing rate constants in the compounds, the ultrafast transient absorption spectra of NI-Py dyads as well as the reference compounds were studied. First, we measured pyrene in a nonpolar solvent, which displayed a positive ESA band at 580 nm, which can be attributed to the transient absorption of the S₂ state (Figure S28). This band decays rapidly and a new positive band rises at 473 nm, which can be attributed to the absorption of the pyrene S_1 state. These dynamics can be ascribed as $S_2 \rightarrow S_1$ internal conversion (IC), which takes about 0.51 ps. No triplet state was observed for pyrene with the fs-TA spectra, which is in agreement with a long fluorescence lifetime of 7.9 ns. For Py-Ph, two ESA bands at 580 and 635 nm appeared after excitation within 0.23 ps (S_2 \rightarrow S_n), and these bands decay rapidly while a broad ESA rise in a range of 465–540 nm in 22 ps ($S_2 \rightarrow S_1$ IC, Figure S29). On later delay times, the S1 state band decays, and a new ESA band centered at 445 nm appears, which is the $T_1 \rightarrow T_n$ transition of the pyrene moiety; this band is similar to the ns-TA spectra of this compound (Figure 8e). These results of pyrene and Py-Ph are in accordance with the previously reported literature.^{59,61,62}

Upon photoexcitation of NI-Py-1 at 350 nm, the transient absorption spectra in DCM were recorded (Figure 9). There are a few ESA bands that appeared in ranges of 400-550 nm and 580-720 nm (Figure 9a). The ESA band increases, and shortly after, it decreases at longer delay times. This shows that the ESA signal includes several excited state processes, for instance, the singlet excited state $(S_1 \rightarrow S_n, \text{ transition})$, radical cation of pyrene (Py+), or radical anion of NI (NI-) absorptions and the triplet state $(T_1 \rightarrow T_w \text{ transition})$. All these excited states show the ESA signals almost in the same range from 400-550 nm, which can well overlap with each other.^{61,63–65} The initial absorption at 465 nm along with a shoulder band at about 550 nm can be attributed to pyrene singlet excited state absorption ($S_1 \rightarrow S_n$, transition). After that, the signal of the pyrene radical cation is intensified in the same range; meanwhile, another broad band centered at 680 nm (the absorption band of $\mathbf{P}\mathbf{y}^{+}$) was developed, indicating the formation of the CS state. Subsequently, with the decay of the CS state, a broad triplet ESA band centered at 464 nm was retained, corresponding to the $T_1 \rightarrow T_n$ transition of the ³Py state, indicating the occurrence of ISC. Note that the ESA bands at 420 and 500 nm of NI⁻⁻ are probably overlapped with the broad ESA bands of Py^+ and ${}^{3}Py$. We assign the broad band at 464 nm at later times to triplet state absorption since it does not decay completely on the time scale of our fs-TA measurements (ca. 5.5 ns). The photophysical process of NI-**Py-1** can be presented as $S_1 \rightarrow {}^1CT \rightarrow {}^3LE$. It is noteworthy to mention here that for both the dyads, we did not observe pyrene higher singlet excited state S_2 (as observed in the case of pristine pyrene and Py-Ph) because of the ultrafast charge separation to form the CS state (via the $S_1 \rightarrow {}^1CT$ path).

To obtained the time constants of the CS and CR processes, global analysis of the transient absorption data was performed, and evolution-associated difference spectra (EADS) were obtained for the description of photodynamic in the dyads (Figure 9b). For NI-Py-1, four time constants were necessary for a satisfactory fit of the data. The initial spectral component represents the population of the singlet excited state in less than 1 ps with the partial ultrafast CS process. The singlet excited state decays within 0.81 ps due to charge separation, the intensity of the ESA band at 465 nm is increased, and a new positive ESA in a range of 580–720 nm rises (evolution from black to red with a lifetime of 82 ps indicates that the charge separation is efficient in the dyad). The broad band

centered at 680 nm is slightly blue-shifted, while the 465 nm band starts decreasing (evolution from red to blue in Figure 9b), which could be due to vibrational cooling. The CR process takes place at a longer time scale (3.0 ns) and produces the long-lived pyrene localized triplet state (evolution from blue to green in Figure 9b). The last component with an infinite lifetime is beyond the range of our fs-TA experiment setup. The selected kinetic traces at 465 and 670 nm are presented in Figure 9c. The transient absorption spectra of NI-**Py-1** measured in ACN show almost similar features to those observed in DCM (Figure S30) but with slower CS (~1.6 ps) and CR (~5.1 ns). Compared with the previously reported perylene-NI dyad in DCM (CS takes 0.66 ps, CR takes 8 ns), these dyads show almost similar CS rate constants, while the CR is slightly faster.⁴⁰

Apart from some differences, NI-Py-2 has similar optical characteristic behaviors in transient absorption spectra to those observed for NI-Py-1 (Figure S31). The broad ESA band from 580 to 720 nm is relatively weak, charge separation occurred upon photoexcitation within 0.23 ps, and the ISC rate was found to be about 3.2 ns. Similar results were observed in ACN with slightly slower kinetics CS of 3.9 ps and ISC of 4.5 ns. The observation of the pyrene radical cation in both the dyads is in good agreement with the spectroelectrochemical measurements (Figure 6c and Figure S21c).

Additionally, we measured the femtosecond transient absorption spectra of NI-Ph derivatives in toluene (Figure 10



Figure 10. Femtosecond transient absorption spectra of (a) **NI-4Ph** at different time delays and (b) decay trace at 514 nm. In toluene. λ_{ex} = 350 nm. 20 °C.

and Figure S32). NI-4Ph initially shows stimulated emission at 420 nm and a sharp ESA band centered at about 514 nm along with a broad tail at about 625 nm, which is assigned to the singlet excited state $(S_1 \rightarrow S_n \text{ transition})$ (Figure 10a). However, these ESA bands first increase, and then after a short time, they start decreasing and blue-shifting; the new ESA band is assigned to the $T_1 \rightarrow T_n$ transition of the ³NI state.⁵⁵ Through single wavelength fitting (Figure 10b), the ISC time constant is determined as ca. 20.1 ps and the excited state dynamics can be summarized as $*S_1 \rightarrow T_4 \rightarrow T_1$. Similarly, for NI-3Ph upon 350 nm photoexcitation, an ESA band at about 465 nm appeared, which became broader at later delay times and extended up to 700 nm; it can be assigned to the triplet excited state absorption of the NI moiety (Figure S32). Thus, in the nonpolar solvents, the triplet excited state of NI-Ph derivatives populates via the enhanced ISC due to the $n \rightarrow \pi^*$ to $\pi \to \pi^*$ transition (singlet/triplet energy level matching).

3.6. Time-Resolved Electron Paramagnetic Resonance (TREPR) Spectroscopy. Previously, the EPR spectra of pyrene were measured in a pyrene-doped fluorene single crystal.⁶⁶ The values of zero-field splitting (ZFS) parameters | *D*| and |*E*| were determined as 2398 and 539 MHz, respectively. However, no TREPR spectrum was supplied. The TREPR spectrum of pyrene in sodium dodecyl sulfate (SDS) aqueous micelle was studied, but the observed signal was assigned to the pyrene cation, generated by two-photon ionization.⁶⁷ Previously, the fluorescence properties of the pyrene-pyrazole nitronyl and imino nitroxides dyads were also studied, but the triplet state and the electron spin polarization of the ISC of the compounds were not studied.⁶⁸

Herein, first, we studied the TREPR spectrum of the triplet state of **Py-Br**, with randomly oriented sample in frozen solution at 80 K (Figure 11a). An electron spin polarization



Figure 11. TREPR spectra of (a) Py-Br, (b) NI-3Br, (c) NI-Py-1, and (d) NI-Py-2, recorded at 80 K in frozen toluene and 400 ns after pulsed laser excitation at 355 nm, 10 mJ per pulse. Positive signal amplitudes represent enhanced absorptive (A) and negative amplitudes stand for emissive (E) polarization of the respective transition. Red lines are computer simulation, and black curves are experimental TREPR spectra.

pattern (*e*, *e*, *e*, *a*, *a*, *a*) was observed, which is typical for the triplet state of an organic chromophore generated by the spinorbit intersystem crossing (SO-ISC).^{27,36,37} The |D| and |E| values were determined as 2350 and 510 MHz, respectively (Table 5). These *D* and *E* values are close to those observed for pyrene when doped in the fluorene crystal.⁶⁶

Table 5. Zero Field Splitting Parameters (D and E) and Triplet-State Population Sublevels (P_x , P_y , and P_z) Obtained from Simulation of the Triplet-State TREPR Spectra of the Compounds

compounds	lDl (MHz)	E (MHz)	$P_{\rm x}$	$P_{\rm y}$	P_{z}	$\frac{ P_{\rm x} - P_{\rm y} }{ P_{\rm z} - P_{\rm y} ^a}$
NI-Py-1	2450	510	0.2	0.8	0	0.75
NI-Py-2	2300	479	0	0	1	0/1
Py-Br	2350	510	0	0.33	0.67	0.97
NI-3Br	2750	120	0	0	1	0/1
NI-4Br ^b	2590	150	0.33	0.67	0	0.50

^{*a*}Unique ratio of populations, which determines the triplet ESP. ^{*b*}Literature values.⁵⁷

With simulation of the TREPR spectrum of **Py-Br**, the population rates of the sublevels of the T₁ state are $P_x:P_y:P_z = 0:0.33:0.67$. The spectrum did not show any shape change along with longer delay times. It should be pointed out that the transient species lifetime determined with the TREPR spectroscopy is about 5 μ s, which is much shorter than the triplet state lifetime ($\tau = 160 \ \mu$ s) of **Py-Br** determined with the nanosecond transient absorption spectroscopy (Figure S25). Spin lattice relaxation (SLR) may contribute to this discrepancy.

No satisfactory triplet TREPR spectrum was obtained for native pyrene due to the low ISC yield ($\Phi_{\Delta} = \sim 30\%$ in HEX). Previously, we reported the TREPR spectrum of the triplet state of **NI-4Br**, for which the ESP is (*e*, *a*, *e*, *a*, *e*, *a*).⁵⁷ The ZFS parameters were determined as |D| = 2590 MHz and |E| =150 MHz, respectively. The population rates of the sublevels of the T₁ state of **NI-4Br** is $P_x:P_y:P_z = 0.33:0.67:0$. For **NI-3Br**, we observed an ESP of (*e*, *e*, *a*, *a*, *a*) (Figure 11b) and almost similar ZFS parameters (|D| = 2750 MHz and |E| = 120 MHz). However, the population rates of the sublevel of the T₁ state of **NI-3Br** are $P_x:P_y:P_z = 0:0:1$, which are drastically different from **NI-4Br**. Furthermore, the $|P_x - P_y|/|P_z - P_y|$ values of **NI-3Br** (0/1) and **NI-4Br** (0.50) are also drastically different from each other (Table 5).

This is an interesting example where the Br atoms attached at different positions of the chromophore may induce different population rates of the sublevels of the T_1 state, i.e., the electron spin selectivities of the bromo-**NI** analogues are different. It is noteworthy to mention here that the *D* parameters of pyrene and **NI** moieties are only slightly different but the *E* parameters are drastically changed. This difference may be useful for the assignment of triplet state localization of the **NI-Py-1** and **NI-Py-2** dyads.

The dyads NI-Py-1 and NI-Py-2 show ISC ability, and thus the triplet state was studied with TREPR spectra (Figure 11c,d). The (a, e, a, e, a, e) ESP features of NI-Py-1 are different from both **Py-Br** and **NI-3Br**, and therefore the ISC mechanism of **NI-Py-1** should be different from the SO-ISC. The |D| and |E| parameters of **NI-Py-1** were determined as 2450 and 510 MHz, respectively. Based on the ZFS parameters, especially the E values, we purpose that the triplet state of **NI-Py-1** is confined to the pyrene moiety. This is in agreement with the ns-TA spectral results (Figure 7a). Interestingly, for **NI-Py-2**, which has different connections to the **NI** moiety, a TREPR spectrum with different ESP (e, e, e, a, a, a) features was observed. Moreover, the population rates of the T₁ state are drastically different from those of **NI-Py-1** (Table 5).

This geometry-dependent feature is typical for the electron donor/acceptor dyads showing the SOCT-ISC mechanism.^{27,38} The T₁ state of **NI-Py-2** should be also confined on the pyrene moiety based on the ZFS *E* parameter (|E| = 479 MHz). The complete simulation parameters of the TREPR spectra are summarized Table 5.

3.7. Computational Study. The ground state geometries of the compounds were optimized with DFT calculations (Figure 12). For NI-Py-1, the dihedral angle between the NI and the perylene moieties is 113.6°, and this is almost similar to the previously reported NI-Py analogue ($\varphi = 107^{\circ}$).⁵⁰ Meanwhile, for NI-Py-2, the torsion about the C–C linker has more freedom, and the dihedral angle is much smaller (54.4°). This result indicates that some extent of electronic coupling is expected between donor and acceptor units being connected



Figure 12. Dihedral angles (in degree) of the compounds at the linkage C–C bonds based on optimized ground state geometries at the B3LYP/6-31G(d) level with Gaussian 09W.

by a C–C single bond, and therefore we observed CT absorption bands in the UV–vis absorption spectra (Figure 1). In comparison, similar torsion angles were observed for the respective reference compounds NI-4Ph (53.7°) and NI-3Ph (36.5°), which indicate larger torsion freedom, as a result of attachment of the smaller phenyl substituents. The different dihedral angles between the two units may result in different electronic coupling, and thus CT absorption bands with different magnitudes were observed for the dyads.

The optimized ground state geometry is not sufficient to investigate the conformational flexibility of the torsion of the electron donor/acceptor mutual orientation. Therefore, we constructed the potential energy surface (PES) of the torsion of the C–C linker between the NI and Py moieties (Figure 13). For NI-Py-1, the PES is rather flat in a dihedral angles



Figure 13. (a) Calculated ground state (S_0) potential energy surface of the compounds as a function of the dihedral angle between the two chromophores. (b) Magnified view of (a) in a low energy range. The straight line in (b) near the bottom shows the room temperature accessible thermal energy range (0.026 eV). Calculations were performed at the (B3LYP/6-31G(d)) level with Gaussian 09W.

range of $60-120^{\circ}$. This range is similar to the recently reported perylene-**NI** dyad $(60-120^{\circ})$.⁴⁰ The geometry accessible at room temperature is mainly in a range of 52–128°.

Interestingly, for NI-Py-2, the potential energy curve is shallow with two energy minima at 56 and 130° with the thermally accessible dihedral angle at room temperature being in a range of $41-74^{\circ}$. However, efficient triplet state production was observed for NI-Py-2. It is well known for SOCT electron donor/acceptor systems that orthogonal geometry is much favorable, but our results imply that other factors may also affect ISC efficiency, i.e., the chromophore orientation or ¹CT and ³LE state energy level matching. The frontier molecular orbitals of the compounds were studied (Figure S33). For both NI-Py-1 and NI-Py-2, the highest occupied molecular orbital (HOMO) is localized on the pyrene moiety and the lowest unoccupied molecular orbital (LUMO) is localized on the NI moiety, indicating that the electron transfer is possible from the pyrene unit to NI unit. However, a minor delocalization of the molecular orbitals was observed, which is responsible for the CT absorption bands (Figure 1). The molecular orbitals of HOMO-1 and LUMO+1 are slightly delocalized, and fully confined molecular orbitals of Py-Ph were also studied, and more delocalized molecular orbitals were found as compared with the dyads.

The triplet state spin density distribution of the dyads at the optimized triplet state was presented (Figure 14a,d). For NI-



Figure 14. Isosurfaces of spin density distribution of NI-Py-1 (upper panel) and NI-Py-2 (lower panel) at the optimized (a and d) triplet state, (b and e) radical anion, and (c and f) radical cation geometries (isovalues are 0.0025). Calculated at the B3LYP/6-31G(d) level using Gaussian 09W.

Py-1, the triplet state is mainly localized on the **Py** moiety but there is also a minor contribution from the **NI** unit. Similarly, triplet state spin density of **NI-Py-2** is localized on the **Py** moiety but the leakage to the **NI** unit is also observed. This is because of relative triplet state energy levels of both the moieties: the triplet energy level of the **Py** moiety is 2.10 eV and the NI triplet energy level is 2.21 eV.^{47,58} This result indicates that upon photoexcitation, the triplet state will be mainly localized on the pyrene moiety, which is in agreement with the ns-TA and TREPR observations (Figures 7 and 11). The electron spin density surfaces of the radical anion and radical cation were also calculated (D₀ states). For both the dyads, the spin density of the radical anion is localized on the **NI** moiety with a small leakage to the **Py** moiety (Figure



^{*a*}The energy levels of the singlet excited states are derived from the spectroscopic data, and CT state energy levels in different polarity solvents are obtained from the CT emission band. The triplet state energy levels are estimated by the TD-DFT method. The numbers in superscripts indicate the spin multiplicity.

14b,e). On the other hand, the electron density of the radical cation is mainly restricted to the **Py** moiety (Figure 14c,f).

As the linkage in NI-Py-1 is at the 4-C position of the NI moiety to the Py unit, thus we expect better electronic communication between the two units. In the case of NI-Py-2, the attachment of the NI moiety is at the 3-C position to Py, which may exert less steric hindrance and give more freedom of rotation. This result further implies that the Py moiety serves as an electron donor and the NI unit is the electron acceptor.

Based on the above studies, the overall photophysical processes of compounds are summarized in Scheme 2. For NI-**4Ph**, the ISC occurs within 20.1 ps via $S_1 \rightarrow T_4$ transition as these states share the same energy level and then followed by IC to the T₁ state. For NI-Py-1, upon pulsed laser excitation, ultrafast charge separation occurs (0.81 ps) to give the ¹CT state. The energy of the CT state is dependent on solvent polarity. For instance, the CT state of NI-Py-1 is 2.80 eV in HEX, whereas it decreased to 2.13 eV in ACN. The energy gap between the CT state and ³LE in different polarity solvents can play an important role in the solvent polarity dependency of the SOCT-ISC efficiency. The subsequent CR (take ~3.0 ns) leads to the formation of the pyrene localized triplet state. According to the DFT calculations and literature values,^{47,50,58} the ³LE of the pyrene moiety should be the lowest laying triplet in the dyads (supported by ns-TA and TREPR). The ISC efficiency of these dyads is moderate in nonpolar solvents and high in polar solvents. This can be due to the high ³LE state energy (2.03 eV) of the pyrene moiety, which is much closer to the ¹CT energy in polar solvents. Similarly, photophysical processes of NI-3Ph and NI-Py-2 are summarized in Scheme S1.

4. CONCLUSIONS

In summary, naphthalimide (NI)-pyrene (Py) compact electron donor-acceptor dyads (NI-Py-1 and NI-Py-2) were prepared to study the effect of mutual orientation of the chromophores on the spin-orbit charge transfer intersystem crossing (SOCT-ISC) efficiency. The synthesis is based on the different connections of the pyrene donor unit to the NI acceptor. The purpose of this study is to explore the SOCT-ISC efficiency of the dyads with different mutual orientations of the donor and acceptor and its effect on the electron spin polarization (ESP) pattern of the triplet state. The photophysical properties of the dyads were studied with steady-state and femtosecond/nanosecond time-resolved transient absorption spectroscopies, time-resolved electron paramagnetic resonance (TREPR) spectroscopy, and density functional theory (DFT) calculations. UV-vis absorption shows a clear charge transfer absorption band, and fluorescence is guenched with increasing the solvent polarity for both the dyads. This indicates that photo-induced charge transfer is efficient. Charge separation occurs upon photoexcitation and the ISC efficiency is solvent polarity-dependent ($\Phi_{\Lambda} = 14-52\%$), which is an indication of the SOCT-ISC mechanism. Different from the previous study, these dyads show moderate to high singlet oxygen quantum yields in solvents with different polarities (from nonpolar to polar). On the other hand, the reference compounds (NI-3Ph and NI-4Ph) show high singlet oxygen production in nonpolar solvents (efficient ISC due to $S_1 \rightarrow T_4$ energy level matching). Furthermore, upon nanosecond pulsed laser excitation, we observed two different excited-state absorption (ESA) features for NI-Py-1 and NI-Py-2 dyads with long-lived triplet states (intrinsic lifetime $\tau_{int} = \sim 220 \ \mu s$) and the triplet state is localized on the pyrene moiety (supported by TREPR data, the ZFS E parameter). The ultrafast CS process (~0.81 ps) and the ISC rate (3.0 ns) are observed by femtosecond transient absorption spectroscopy. With TREPR spectroscopy, we confirmed the SOCT-ISC mechanism, and interestingly, the observed ESP pattern is chromophore orientation-dependent and the population rates of the triplet sublevels of the dyad are drastically different from the spin-orbit coupling induced ISC (for monobrominated pyrene and NI). Moreover, the population rates of triplet sublevels are also different with different substitution positions of the Br atom in bromo-NI analogues. The ZFS D and Eparameters clearly indicate that the triplet state of the dyads is confined on the pyrene moiety. Our results are useful for an indepth understanding of the photophysics of compact electron donor-acceptor dyads and helpful for the designing of new heavy atom-free triplet photosensitizers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.1c03537.

Experimental methods, characterization data, cyclic voltammetry, additional steady-state UV-Vis absorp-

tion, luminescence, nanosecond and femtosecond transient absorption spectroscopic data, and additional DFT calculation details (PDF)

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Notes

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