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Anthracene-Naphthalenediimide Compact Electron Donor/Acceptor Dyads: Electronic Coupling, Electron Transfer and Intersystem Crossing

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Abstract: We attached different electron donors of phenyl, anthryl and alkylamino moiety, to electron acceptor naphthalenediimide (NDI) to construct compact electron donor/acceptor dyads. The purpose is to study the effect of electron coupling (the magnitude is the matrix element, V_{DA}) on the photophysical properties of UV-vis absorption, fluorescence emission, especially spinorbit charge transfer intersystem crossing. We found that the magnitude of V_{DA} depends on the electron donating strength of the aryl moieties ($V_{DA} = 0.22 \text{ eV} \sim 0.55 \text{ eV}$), as well as the molecular conformation, based on steady state and time-resolved transient absorption spectroscopies. We also found that electron coupling does not show the add-up (or synergetic) effect. Solvent polarity-dependent intersystem crossing (ISC) was observed for the dyad/triads and singlet oxygen quantum yield decreases in polar solvents. Femtosecond transient absorption results indicate that the charge separation (CS) for 9-An-NDI-NH occurs on time scale of 0.83 ps (in toluene) or 0.71 ps (in acetonitrile). The charge recombination (CR) process (50 ps in toluene) produces triplet state with $\Phi_{ISC} = 19\%$. This result indicates that orthogonal geometry for a compact electron donor/acceptor does not lead to efficient ISC via CR. Other factors such as the energy gap between the CS state and triplet state also determine the ISC efficiency.

1. INTRODUCTION

Tuning the photophysical properties of organic chromophores by molecular structure modification is pivotal for designing of functional organic materials,¹ for instance the photosensitizers for photovoltaics,^{2,3} artificial photosynthesis,^{4,5} photodynamic therapy (PDT),^{6–9} novel biosensors,^{10–12} and triplet-triplet-annihilation upconversion (TTA UC), etc.^{13–21}

Concerning this aspect, two popular approaches are available for tuning the photophysical properties of organic chromophores, one is introducing electron donating or withdrawal groups

to the π -conjugation framework.^{22,23} In this case the absorption and fluorescence emission feature of a chromophore can be changed substantially.²⁴ Another approach is to connect different chromophores together, with a non-conjugation linkage (dyad, triads, etc.). In this case the two components connected are in supramolecular feature, the two components retain their own property at the ground state. With this method, light-harvesting molecular polyads were developed.^{25,26} In general, there exist strong electronic coupling (the magnitude is electronic coupling matrix elements, V_{DA}) between the different units for the first method.¹ However, for the second approach, the geometry or mutual orientation and the distance between the two units can affect the interaction, and normally the interaction between the two units is weak.^{4,5}

Actually, another method exists for tuning the photophysical properties of the organic chromophores. *i.e.* to construct a molecular system, in which there is weak to moderate electronic couplings between the electron donor and acceptors.^{1,4,5,27} This method is unique in the sense that new absorption bands can be resulted,¹ for instance, the charge transfer (CT) absorption band. This feature is different from the fully coupled systems, which usually give a new narrow absorption band, but with the disappearance of the original absorption bands of the respective chromophores. More importantly, this method offers the possibility to tune the intersystem crossing (ISC) property of the heavy atom-free chromophores, by employing the ISC channel of the charge recombination (CR), or by the hyperfine coupling interaction (HFI), *i.e.* the radical-pair ISC (RP-ISC).^{4,5,27} However, the CR induced triplet formation attracted much less attention until now.

Concerning ISC, compact electron donor/acceptor dyads, *i.e.* the electron donor and acceptor are connected with short linker or directly linked together, are with large *J* values, thus the HFI is non-sufficient to ensure efficient ISC, usually the ISC of such compact dyads is non-efficient.^{4,5}

Recently it was found the spin-orbit charge transfer intersystem crossing (SOCT-ISC) occurs for electron donor/acceptor systems with strong coupling, given the electron donor and acceptor are in orthogonal geometry (in other words, π planes are in perpendicular geometry).^{28–34} As a result, the molecular angular momentum changes generated during CR can compensate the electron spin angular momentum changes for ISC, thus the CR is accompanied with electron spin flip, *i.e.* the ISC is greatly enhanced. This is in particular interest for preparation of heavy atom-free organic triplet photosensitizers, and the molecular structure can be greatly simplified, as compared to other heavy atom-free triplet photosensitizers, such as those based on symmetry breaking charge transfer dyads,^{35,36} exciton coupling,^{37,38} or those based on electron spin converters.^{39–42} However, the examples for SOCT-ISC are still limited, and the chromophores used for SOCT-ISC are limited to pyrene,²⁸ acridine,²⁹ and anthracene.³⁰ Recently Bodipy unit was used for SOCT-ISC studies.^{31–34,43} However, It is clear that more molecular structures need to be studied for elucidation of the molecular structure-ISC property for the SOCT-ISC molecular systems.

Concerning these aspects, naphthalenediimide (NDI) is interesting for its excellent photo- and chemo- stability, feasible derivatization chemistry, and interesting photophysical properties.⁴⁴⁻⁴⁶ Previously NDI was used for molecular dyads/triads with very weak electronic coupling,²⁷ but it was not used for compact electron donor/acceptor dyads, and it was not used for study of SOCT-ISC.^{28–34} Herein NDI was selected as a light absorption chromophore (also the electron acceptor) to construct compact electron donor/acceptor dyads. NDI is a strong electron acceptor,^{47–50} which favors electron transfer. Different aryl moieties, such as phenyl, anthryl and arylamine, are used as electron donor.⁵¹ In the case of anthryl electron donor, different conformation was achieved by connection at either the 9- or 2- position of the anthryl moiety, as such the V_{DA} was varied

because the dihedral angel between the two parts are different (Scheme 1).³⁰ The electron coupling between the electron donors and the NDI moiety, as well as its effect on the UV–vis absorption and emission properties, were studied with various steady state and time-resolved transient spectroscopies. SOCT was observed for the days attached with anthryl moiety and the SOCT-ISC efficiency is highly dependent on the solvent polarity. We found that the orthogonal geometry is not the only requirement for efficient ISC. The results may be useful for study of the ISC via CR, a ubiquitous process for organic photovoltaics and artificial photosynthesis.

2. Experimental Section

2.1. General Methods. All the chemicals used in synthesis are analytical pure and were used as received. Fluorescence quantum yields were measured in toluene. For **NDI**, anthracene ($\Phi_F = 27\%$ in ethanol) was used as reference, for the other compounds, diiodobodipy ($\Phi_F = 2.7\%$ in CH₃CN) was used as reference. The structures of diiodoBodipy is shown in Scheme 1. The fluorescence lifetimes of the compounds were measured with OB920 luminescence lifetime spectrometer (with TCSPC detection mode. Edinburgh Instrument Ltd., UK). For **NDI**, the fluorescence lifetimes were measured with 340 nm EPL picosecond pulsed laser (pulse width: 800 ps, maximum average power: 40 μ W). For **Ph-NDI-NH**, **Br-NDI-NH**, **2-An-NDI-NH** and **9-An-NDI-NH**, the luminescence lifetime were measured with 445 nm EPL picosecond pulsed laser (pulse width: 70 ps, maximum average power: 5 mW). Fluorescence spectra were recorded with a RF 5301PC spectrofluorometer (Shimadzu, Japan).

2.2. Synthesis of NDI. 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA) (670 mg, 2.5 mmol) was added in freshly distilled DMF (5 mL) at room temperature, then 2-ethylhexylamine (970 mg, 7.5 mmol) was added to the above slurry. The slurry was heated at 140 °C for

overnight under nitrogen (N₂) atmosphere. This mixture was then cooled to room temperature and poured into cold water (100 mL). The precipitate was collected with filtration and washed with water. After drying under vacuum, the solid was further purified by column chromatography (silica gel; DCM/petroleum ether, 1:1, v/v) to give the product as a white solid. Yield: 545 mg, 42.0%. ¹H NMR (CDCl₃, 400 MHz): 8.76 (s, 4H), 4.20–4.10 (m, 4H), 1.97–1.91 (m, 2H), 1.38–1.25 (m, 16H), 0.96–0.88 (m, 12H). TOF–HRMS ([C₃₀H₃₈N₂O₄]⁺): calcd m/z =490.2832, found m/z = 490.2821.

2.3. Synthesis of 2Br-NDA. A mixture of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA) (5.00 g, 18.64 mmol) and oleum (20% SO₃, 75 mL) was stirred at room temperature. Iodine (60 mg, 0.24 mmol) and bromine (5.96 g, 37.3 mmol) were then added to the above mixture. The resulting mixture was heated at 50 °C for 48 h. After cooling to room temperature, the mixture was poured into cold water (100 mL). The precipitate was collected with filtration and washed with water. After drying under vacuum, 6.19 g yellow solid was obtained. This crude product was used for the next step of the synthesis without further purification.

2.4. Synthesis of 2Br-NDI. Under N₂ atmosphere, the mixture of 2Br-NDA (1.06 g, 2.5 mmol), 2-ethylhexylamine (968 mg, 7.5 mmol) and acetic acid (25 mL) was stirred at 120 °C for 2 h. After cooling to room temperature, the mixture was poured into cold water (100 mL). The precipitate was collected with filtration and washed with water (3 × 50 mL) and methanol (3 × 50 mL). After drying under vacuum, the reddish solid was purified by column chromatography (silica gel; CH₂Cl₂/petroleum ether, 1:1, v/v). A yellow solid was obtained. Yield: 524 mg, 31.0%. ¹H NMR (CDCl₃, 400 MHz): 9.00 (s, 2H), 4.15 (t, J = 5.9 Hz, 4H), 1.94 (s, 2H), 1.39–1.29 (m, 16H), 0.95–0.88 (d, 12H). TOF–HRMS ([C₃₀H₃₆N₂O₄Br₂]⁺): calcd m/z = 646.1042, found m/z = 646.1030.

2.5. Synthesis of Bis-Ph-NDI. Under N₂ atmosphere, a solution of sodium carbonate (25 mg, 0.24 mmol) in distilled water (1 mL) was added to a solution of phenylboronic acid (43 mg, 0.36 mmol), **2Br-NDI** (52 mg, 0.08 mmol) in 1,4-dioxane (3 mL) and then tetrakis(triphenyl-phosphane)palladium (1 mg, 0.0008 mmol) was added after the above solution was degassed with N₂ for 30 min. The mixture was stirred at reflux for 14 h under N₂. After cooling to room temperature, a solution of sodium sulfite (1.0 g) in water (10 mL) was added to the reaction mixture. The mixture was extracted by DCM and dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure and the residue was purified by chromatography (silica gel; DCM/petroleum ether, 1:1, v/v). A yellow solid was obtained. Yield: 5 mg, 10.0%. ¹H NMR (CDCl₃, 400 MHz): 8.66 (s, 2H), 7.54–7.48 (m, 6H), 7.42–7.40 (m, 4H), 4.03 (d, *J* = 8 Hz, 4H), 1.91–1.85 (m, 2 H), 1.35–1.26 (m, 16H), 0.97–0.86 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): 162.9, 162.6, 147.7, 140.5, 135.9, 128.4, 128.3, 128.1, 127.2, 125.6, 123.0, 44.4, 37.7, 30.6, 28.5, 23.9, 23.1, 14.1, 10.6. TOF–HRMS ([C4₂H₄₆N₂O₄]⁺): calcd *m/z* = 642.3458, found *m/z* = 642.3434.

2.6. Synthesis of Br-NDI-NH. Under N₂ atmosphere, a mixture of 2Br-NDI (488 mg, 0.75 mmol), 2-ethylhexylamine (284 mg, 2.2 mmol), and 2-methoxyethanol (3 mL) was stirred at 120 °C for 6 h. After cooling to room temperature, water was added to the mixture and then the mixture was extracted with DCM. After removing the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel; DCM/petroleum ether, 1:1, v/v). A red solid was obtained. Yield: 246 mg, 47.0%. ¹H NMR (CDCl₃, 400 MHz): 10.19 (t, J = 5.4 Hz, 1H), 8.87 (s, 1H), 8.30 (s, 1H), 4.18–4.10 (m, 4H), 3.50 (t, J = 5.8 Hz, 2H), 1.96–1.90 (m, 2H), 1.80–1.77 (m, 1H), 1.57–1.29 (m, 24H), 1.01–0.87 (m, 18H). TOF–HRMS ([C₃₈H₅₄N₃O₄Br]⁺): calcd m/z = 695.3298, found m/z = 695.3317.

2.7. Synthesis of 9-An-NDI-NH. 9-An-NDI-NH was prepared with a method similar to that used for **Bis-Ph-NDI**, except the molar ratio of the 9-anthraceneboronic acid and **Br-NDI-NH** is 2:1. A red solid was obtained. Yield: 8 mg, 15.0%. ¹H NMR (CDCl₃, 400 MHz): 10.29 (t, J = 5.2 Hz, 1H), 8.55 (d, J = 9.9 Hz, 2H), 8.39 (s, 1 H), 8.08 (d, J = 8.4 Hz, 2H), 7.43 (t, J = 8.5 Hz, 2H), 7.33 (d, J = 9.5 Hz, 2H), 7.23 (d, J = 9.2, 2H), 4.20–4.10 (m, 2H), 3.80 (d, J = 7.4 Hz, 2H), 3.58 (t, J = 5.9 Hz, 2H), 2.02–1.94 (m, 1H), 1.85–1.82 (m, 1H), 1.64–1.30 (m, 18H), 1.11–1.01 (m, 9H), 0.97–0.86 (m, 10H), 0.74–0.66 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz): 166.8, 163.2, 162.2, 152.5, 137.8, 136.7, 135.6, 134.1, 133.5, 131.5, 131.4, 129.4, 128.8, 128.3, 127.2, 126.8, 125.7, 125.6, 125.5, 125.0, 123.2, 120.4, 120.3, 100.1, 46.5, 44.0, 43.9, 39.4, 37.8, 37.5, 31.2, 30.7, 30.3, 28.9, 28.6, 28.4, 24.6, 24.0, 23.8, 23.1, 23.0, 22.9, 14.1, 14.0, 14.0, 11.0, 10.7, 10.5. TOF–HRMS ([C₅₂H₆₃N₃O₄]⁺): calcd m/z = 793.4819, found m/z = 793.4837.

2.8. Synthesis of Bis-2-An-NDI. Bis-2-An-NDI was prepared with a method similar to that used for Bis-Ph-NDI but the molar ratio of the 2-anthraceneboronic acid and **2Br-NDI** is 4:1. A dark blue solid was obtained. Yield: 16 mg, 30.0%. ¹H NMR (CDCl₃, 400 MHz): 8.86 (s, 2H), 8.50 (s, 4H), 8.13 (s, 2H), 8.09–8.04 (m, 6H), 7.53–7.51 (m, 4H), 7.45 (d, J = 1.6 Hz, 1H), 7.44 (d, J = 1.6 Hz, 1H), 4.11–4.03 (m, 4H), 1.94–1.88 (m, 2H), 1.37–1.30 (m, 12H), 0.91–0.84 (m, 16H). ¹³C NMR (CDCl₃, 100 MHz): 163.0, 162.7, 147.5, 137.8, 136.3, 132.3, 132.1, 131.5, 130.9, 128.3, 127.7, 127.3, 127.1, 126.6, 126.4, 125.8, 125.7, 125.6, 123.0, 44.5, 37.7, 30.6, 29.7, 28.5, 23.9, 23.1, 14.1, 10.6. TOF–HRMS ([C₅₈H₅₄N₂O₄]⁺): calcd m/z = 842.4084, found m/z = 842.4077.

2.9. Synthesis of Ph-NDI-NH. Ph-NDI-NH was prepared with a method similar to that used for **Bis-Ph-NDI**, except the molar ratio of the phenylboronic acid and **Br-NDI-NH** is 3:1. A yellow solid was obtained. Yield: 29 mg, 60.0%. ¹H NMR (CDCl₃, 400 MHz): 10.19 (t, J = 5.2

Hz, 1H), 8.51 (s, 1H), 8.31 (s, 1H), 7.48–7.40 (m, 3H), 7.35 (m, 2H), 4.20–4.10 (m, 2H), 4.06– 3.97 (m, 2H), 3.52 (t, J = 5.8 Hz, 2H), 2.00–1.77 (m, 3H), 1.58–1.52 (m, 2H), 1.51–1.46 (m, 2H), 1.40–1.21 (m, 20H), 1.00 (t, J = 7.4 Hz, 3H), 0.94–0.84 (m, 15H). ¹³C NMR (CDCl₃, 100 MHz): 166.6, 163.3, 163.1, 152.2, 141.5, 141.2, 135.5, 128.4, 128.3, 128.1, 127.6, 123.0, 122.5, 120.3, 120.2, 99.9, 46.4, 44.3, 43.9, 39.4, 37.8, 37.7, 31.2, 30.7, 30.6, 28.8, 28.8, 28.6, 28.5, 24.5, 24.0, 23.9, 23.1, 23.0, 14.1, 14.1, 14.0, 11.0, 10.7, 10.6. TOF–HRMS ([C44H₅₉N₃O₄]⁺): calcd m/z =693.4506, found m/z = 693.4522.

2.10. Synthesis of 2-An-NDI-NH. 2-An-NDI-NH was prepared with a method similar to that used for **Bis-Ph-NDI**, except the reaction ratio of the 2-anthraceneboronic acid and **Br-NDI-NH** is 2:1 and finally obtained as a red solid. Yield: 36 mg, 65.0 %. ¹H NMR (CDCl₃, 400 MHz): 10.21 (t, J = 7.0 Hz, 1H), 8.67 (s, 1H), 8.44 (s, 2H), 8.32 (s, 1H), 8.03 (d, J = 8.9 Hz, 2H), 8.00 (d, J = 6.4 Hz, 2H), 7.50–7.46 (m, 2 H), 7.38 (dd, $J_1 = 1.6$, $J_2 = 8.7$ Hz, 1H), 4.23–4.11 (m, 2H), 4.05–4.00 (m, 2H), 3.53 (t, J = 5.8 Hz, 2H), 1.99–1.93 (m, 1H), 1.89 (t, J = 5.8 Hz, 1H), 1.85–1.78 (m, 1H), 1.59–1.29 (m, 24H), 1.01 (t, J = 8.5 Hz, 3H), 0.96–0.92 (m, 6H), 0.91–0.84 (m, 9H). ¹³C NMR (CDCl₃, 100 MHz): 166.6, 163.3, 163.1, 152.2, 141.3, 138.6, 135.9, 132.0, 132.0, 131.7, 130.8, 129.1, 128.2, 127.3, 127.2, 126.8, 126.7, 126.2, 125.4, 123.0, 122.7, 120.5, 120.3, 99.9, 46.5, 44.4, 43.9, 39.4, 37.8, 37.8, 31.2, 30.7, 30.6, 29.7, 28.8, 28.6, 28.6, 24.5, 24.1, 23.9, 23.1, 23.0, 14.1, 14.1, 14.0, 11.0, 10.7, 10.6. TOF–HRMS ([C₅₂H₆₃N₃O₄]⁺): calcd m/z = 793.4819, found m/z = 793.4830.

2.11. Singlet Oxygen Quantum Yield (Φ_{Δ}). 1,3-Diphenylisobenzofuran (DPBF) was used as ${}^{1}O_{2}$ scavenger. The ${}^{1}O_{2}$ production was monitored by following the absorbance of DPBF at 414 nm. To determine the singlet oxygen quantum yield (Φ_{Δ}), a relative method was used according to Eq. (1):

$$\Phi_{\rm sam} = \Phi_{\rm std} \left(\frac{1 - 10^{-A_{\rm std}}}{1 - 10^{-A_{\rm sam}}} \right) \left(\frac{m_{\rm sam}}{m_{\rm std}} \right) \left(\frac{\eta_{\rm sam}}{\eta_{\rm std}} \right)^2$$
(Eq. 1)

where 'sam' and 'std' represent the sample and the standard. Φ , A, m and η represent the singlet oxygen quantum yield, the absorbance at excitation wavelength, the slope of the absorbance of DPBF changing over time, and the refractive index of the solvent used for measurement, respectively. Optically matched solutions were used (the solutions of the sample and the standard give same absorbance at the excitation wavelength). Singlet oxygen quantum yields (Φ_{Δ}) were measured in different solvents. For NDI, **Bis-Ph-NDI**, **Bis-2-An-NDI**, the excitation is at 358 nm (S₀ \rightarrow S₁ band, A = 0.215). The monochromatic light source includes a xenon lamp and a monochromator. Phenazine was used as standard ($\Phi_{\Delta} = 0.83$ in benzene) for NDI and anthracene was used as standard ($\Phi_{\Delta} = 0.70$ in methanol) for other compounds; For **Ph-NDI-NH**, **Br-NDI-NH**, **2-An-NDI-NH** and **9-An-NDI-NH**, the excitation is at 496 nm (S₀ \rightarrow ¹CT band, A = 0.223) and 2,6-diiodo-bodipy was used as standard ($\Phi_{\Delta} = 0.85$ in toluene).

2.12. Triplet State Quantum Yield (\Phi_T). To determine the triplet state quantum yield with nanosecond transient absorption spectroscopy, a ground state bleaching method was used and the Φ_T was calculated according to:

$$\Phi_{\rm sam} = \Phi_{\rm std} \left(\frac{\varepsilon_{\rm std}}{\varepsilon_{\rm sam}} \right) \left(\frac{\Delta A_{\rm sam}}{\Delta A_{\rm std}} \right)$$
(Eq. 2)

In the above equation, 'sam' and 'std' represent the sample and the standard. Φ , ε and ΔA respectively represent the triplet quantum yield, the molar absorption coefficient at steady state and the change of optical density (absorbance) of bleaching band in nanosecond transient

 absorption spectroscopy. Optically matched solutions were used (the solutions of the sample and the standard give same absorbance at the excitation wavelength). Diiodo-bodipy in toluene was used as standard ($\Phi_T = 88\%$).

2.13. Nanosecond Transient Absorption Spectroscopy. The nanosecond transient absorption spectra were studied with LP980-K Laser Flash Photolysis Spectrometer (Kinetic mode, Edinburgh Instruments, UK). The analogue signal was digitized with a Tektronix TDS 3012C oscilloscope. The samples were bubbled with N₂ for 15 min and excited with a nanosecond pulsed laser (OpoletteTM, the wavelength is tunable in the range of 210 – 2400 nm. OPOTEK, USA).

2.14. Femtosecond Transient Absorption and Fluorescence Up-conversion Spectroscopy. The femtosecond transient absorption spectra were measured by a pump-probe setup described in detail previously.⁵² Briefly, the amplified pulse is with wavelength of 800 nm and duration of 35 fs, repetition rate 1 kHz and average power 4 W (Spitfire Ace, Spectra-Physics). The output beam was split into two parts, 90% was converted into UV-VIS-IR in the range of 240 - 2400 nm radiation using an optical parametric amplifier (Topas, Light Conversion) and used as pump beam. The left 10% output beam was used to generate a white light continuum (WLC) in a 3 mm thickness rotated CaF₂ plate, and used as a probe beam. The weak probe beam passed through a variable delay line (up to 6 ns) and its absorbance change in the presence and in the absence of the pump beam is measured. The polarizations between pump and probe beams were set at magic angle 54.7° in order to avoid rotational depolarization effects. The entire setup was controlled by a PC with the help of LabView software (National Instruments). Global target analyses were carried out using Glotaran software.⁵³

The fluorescence lifetimes were recorded with a time-resolved fluorescence upconversion spectrometer (Newport) in combination with a mode-locked Ti-sapphire laser (Mai Tai DeepSee, Spectra-Physics). Briefly, the femtosecond laser system generated light pulses at 800 nm of duration 150 fs at a repetition rate 80 MHz and average power 2.9 W. The frequency of the laser pulse was doubled with a BBO crystal and used for excitation (400 nm). The residual 800 nm fundamental pulse was served as a gate beam. All measurements were performed at room temperature under aerated conditions.

2.15. Theoretical Computations. The spin density surfaces of the compounds were calculated based on the DFT//B3LYP/6-311G(d, p)-optimized ground state geometries. The Gaussian 09W program package was used for the calculations.⁵⁴

3. RESULTS AND DISCUSSION

3.1. Design and Synthesis of the Compounds. Firstly we designed **Bis-Ph-NDI** and **Bis-2-An-NDI** (scheme 1), in which phenyl and anthryl moieties were used as electron donors. Anthryl moiety (HOMO energy level is -5.47 eV) is a stronger electron donor than the phenyl moiety (HOMO energy level is -6.69 eV), which were obtained by DFT calculation. Thus we expect more significant electronic coupling between the door and acceptor in **Bis-2-An-NDI** than **Bis-Ph-NDI**. We also prepared mono-amino substituted derivatives with extra Br, phenyl, 9-anthryl and 2-anthryl moieties attached (Scheme 1). The coupling of the amino moiety or the phenyl, anthryl moiety with the NDI moiety was compared. The aim of preparation of **9-An-NDI-NH** and **2-An-NDI-NH** is to study the effect of anthryl substitution on the photophysical properties of the two compounds. The attempt to prepare an analogue of **Bis-2-An-NDI** with connection of 9-position of the anthryl was unsuccessful.

The synthesis is mainly based on Pd(0) catalyzed Suzuki-Miyaura cross coupling reaction. The compounds were obtained with satisfying yields. The molecular structures are fully verified with ¹H NMR, ¹³C NMR and HRMS (see Experiment Section).

Scheme 1. Synthesis of NDI Derivatives ^a



^{*a*} Key words: (a) 2-ethylhexylamine, distilled DMF, N₂, 140 °C for overnight, yield: 42.0%; (b) Br₂, oleum (20% SO₃), 50 °C, 48 h, yield: 78.0%; (c) 2-ethylhexylamine, 120 °C, N₂, 4 h, yield: 31.0%; (d) (f) (g) (h) (i) Arylboronic acid, Pd(PPh₃)₄, Na₂CO₃, 1,4-dioxane/H₂O, N₂, 85 °C for overnight, yield are 10.0 %, 15.0%, 30.0%, 60.0% and 65.0%, respectively; (e) 2-ethylhexylamine, 1,2-dimethoxyethane, 120°C, N₂, 6 h, yield: 47.0%.

3.2. UV–Vis Absorption and Fluorescence Emission Spectra. The UV–Vis absorption spectra of the parent compounds NDI, Bis-Ph-NDI and Bis-2-An-NDI were compared (Figure 1a). NDI gives structured absorption band in the range of 350 - 400 nm. For Bis-Ph-NDI, an extra broad shoulder absorption at 421 nm was observed. This band is assigned to charge transfer (CT) absorption (S₀ \rightarrow ¹CT transition). For Bis-2-An-NDI, a distinct broad absorption band at 524 nm was observed. Moreover, the absorption profiles in the < 400 nm UV region are similar for the three compounds. The broad band at 421 nm and 524 nm are assigned as the CT absorption bands.¹ Based on the observations, we conclude that both the Bis-Ph-NDI and Bis-2-An-NDI show strong electronic coupling between the electron donor and acceptor. It should be pointed that the CT absorption band should not be sensitive to solvent polarity. CT state is formed via the electronic coupling between the donor and acceptor, S₀ \rightarrow ¹CT is an allowed transition, and it is manifested by the CT absorption band in the UV–Vis absorption spectrum. This is different from the charge separated state formed after photoexcitation. In this case the



Figure 1. UV-vis absorption spectra of (a) NDI, Bis-Ph-NDI and Bis-2-An-NDI; (b) Br-NDI-NH, Ph-NDI-NH, 2-An-NDI-NH and 9-An-NDI-NH; $c = 1.0 \times 10^{-5}$ M in toluene. 20 °C.

direct $S_0 \rightarrow {}^1CT$ is forbidden, and these is no such CT absorption band (this is the case for the photo-induced electron transfer systems).

To quantitatively compare the probability of the $S_0 \rightarrow {}^1CT$ transition of the molecules, the transition dipole moments (M_{abs}) of $S_0 \rightarrow {}^1CT$ transition were calculated using the equation 3:¹

$$\left|M_{\rm abs}\right|^2 = \frac{3\ln 10}{8\pi^3 N_A} \frac{hc}{n\tilde{v}_{\rm abs}} \int_{\rm band} \mathcal{E}\left(\tilde{v}\right) d\tilde{v}$$
(Eq. 3)

where $\varepsilon(\tilde{\nu})$ is the molar absorption coefficient in the wavenumber scale, in M⁻¹ cm⁻¹; $\tilde{\nu}_{abs}$ is the maximum of the S₀ \rightarrow ¹CT transition band, in cm⁻¹; N_A is the Avogadro constant, in mol⁻¹; h [erg s] is the Plank constant, in erg s; c is the speed of light, in cm s⁻¹ and n is the refractive index of the solvent respectively. The M_{abs} of **Bis-Ph-NDI** and **Bis-2-An-NDI** were calculated as 2.38 Debye and 2.91 Debye, respectively (Table 1), indicating that both phenyl and anthryl moiety favor the S₀ \rightarrow ¹CT transition. However, the M_{abs} of **Ph-NDI-NH**, **2-An-NDI-NH** and **9-An-NDI-NH** is little smaller than **Br-NDI-NH**, indicating that both phenyl and anthryl moiety do not favor S₀ \rightarrow ¹CT transition as compared with amino moiety in **Br-NDI-NH**, thus the amino-containing compounds give more significant CT absorption band.

Ganguly et al. used Hush equation 4 to calculate the electronic coupling matrix element (V_{DA}) in neutral donor/acceptor systems.⁵⁵ From the charge transfer absorption band in these NDI derivatives (Figure 1a), the electronic coupling matrix element (V_{DA}) were calculated according to eq. 4 and the data are presented in table 1.

$$V_{\rm DA}(\rm cm^{-1}) = \left(\frac{2.06 \times 10^{-2}}{R}\right) \left(\varepsilon_{\rm max}^{\rm CT} v_{\rm max}^{-\rm CT} \Delta v_{1/2}^{-\rm CT}\right)^{1/2}$$
(Eq. 4)

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where *R* is the separation between the center of electron donor and acceptor, in Å; \mathcal{E}_{max}^{CT} is the molar absorption coefficient at the maximum of the CT absorption band, in [M⁻¹ cm⁻¹]; v_{max}^{-CT} is the absorption maximum of the CT absorption band in wavenumber scale, in cm⁻¹; $\Delta v_{1/2}^{-CT}$ is the full width of the band at the half maximum, in cm⁻¹. The distance between the center of the donor and acceptor, which determined by DFT optimization of the geometry, was used as upper limit distance. Herein, $R_{Br-NDI-NH} = 3.92$ Å, $R_{9-An-NDI-NH} = 5.59$ Å, $R_{2-An-NDI-NH} = 7.59$ Å, $R_{Bis-Ph-NDI} = 5.48$ Å and $R_{Bis-2-An-NDI} = 7.59$ Å are used to estimated V_{DA} .

The electronic coupling matrix elements (V_{DA}) of **Bis-Ph-NDI** and **Bis-2-An-NDI** were calculated as 0.34 eV and 0.22 eV, respectively (Table 1). The V_{DA} of **Bis-2-An-NDI** is smaller than **Bis-Ph-NDI**, even though **Bis-2-An-NDI** has a larger value of the transition dipole moments (M_{abs}). The main reason is that the smaller size of benzene ring decreases donor's distance, which finally reduces the separation between the center of electron donor and acceptor in **Bis-Ph-NDI** ($R_{Bis-Ph-NDI} = 5.48$ Å and $R_{Bis-2-An-NDI} = 7.59$ Å).

Most amino-substituted NDI compounds have two absorption bands. The one bellowed 400 nm is assigned to the unsubstituted naphthalenebisimides and another broad long-wavelength band in visible region is assigned to charge transfer transition, which was well demonstrated by Würthner and coworkers.^{56,57} This two absorption bands were labeled with $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transition, respectively. Herein, amino-substituted NDI derivatives with extra electron donor, such as phenyl, anthryl, were studied.

The UV–Vis absorption of mono amino-substituted NDI derivatives was presented in Figure 1b. These compounds share a common significant CT band at ca. 570 nm. The results are interesting, since the presence of anthryl moiety in **2-An-NDI-NH** and **9-An-NDI-NH** does not increase the CT band magnitude, although it exerts significant effect on the UV–Vis absorption

of **Bis-2-An- NDI** (Figure 1a). Based on the CT absorption bands, the V_{DA} values of the complexes ware calculated (Table 1). The result in Figure 1b show that with the mono-amino substitution on the NDI moiety, the anthryl moiety exerts minor effect on the magnitude of the CT band. In other words, there is no add-up effect (or synergic effect) for the electronic coupling between the electron donor and acceptor, given the two electron donors in the triad are with different electron donating ability. In comparison of the electron donating ability, the HOMO of anthracene is with energy level of -5.47 eV, the HOMO energy level of the amine moiety is -6.25 eV. Hence the anthracene moiety should be the main electron donor and acceptor.

It should be pointed out that for the Bodipy-anthracene dyads,^{31,32} the electronic coupling between the electron donor and acceptor is weak, thus there is no CT absorption band (i.e. there is no adiabatic CT). But upon photoexcitation of the Bodipy-anthracene dyad, there will be non-adiabatic CT, i.e. the PET process.

The fluorescence emission property of the compounds was studied (Figure 2). **NDI** is known to show very weak fluorescence due to efficient ISC.⁵⁸ However, much stronger fluorescence was observed in toluene. One possible reason is the formation of exciplexes of **NDI** with toluene, which was proved by monitoring the emission of the compound in *n*-hexane in presence of different equivalent of toluene.

The emission of these proposed exciplexes was also observed in *o*-xylene and *p*-xylene (Supporting information, Figure S24). **Bis-Ph-NDI** and **Bis-2-An-NDI** do not show similar band as that of **NDI** (Figure 2a). Previously the exciplex or CT complex emission of NDI with toluene or xylene were observed with coordination framework materials, but not in solution phase.^{59,60} The amino-containing derivatives such as **Br-NDI-NH** and **Ph-NDI-NH** show intense emission

at ca. 570 nm.⁶¹ Other amino-substituted NDI derivatives such as **2-An-NDI-NH** and **9-An-NDI-NH** give emission at similar wavelength (Figure 2b), but the emission intensity is weaker. The emission is structureless and is assigned to CT band.



Figure 2. Fluorescence emission spectra of (a) NDI; Bis-Ph-NDI and Bis-2-An-NDI (A = 0.126), $\lambda_{ex} = 340$ nm, the asterisk "*" designates the Raman scattering peak of the solvent molecules; (b) Br-NDI-NH, Ph-NDI-NH, 2-An-NDI-NH and 9-An-NDI-NH (A = 0.035), $\lambda_{ex} = 470$ nm. Optically matched solutions were used. In toluene. 20 °C.

The amino-substituted NDI derivatives shows red-shifted emission in polar solvents (Supporting information, Figure S25a). For **Br-NDI-NH**, the fluorescence intensity does not vary significantly in different solvents (Supporting information, Figure S25b), which is not the typical feature of the molecules with photo-induced electron transfer (PET). For **Ph-NDI-NH** and **2-An-NDI-NH** (Figure 3a and 3b), however, a clear trend of fluorescence quenching was observed in polar solvents. This quenching effect in polar solvents for **Ph-NDI-NH** is attributed to charge-transfer character of S₁ state and for **2-An-NDI-NH** the electron transfer from the anthryl moiety to the NDI moiety.⁶² In comparison, no clear quenching effect was observed for **9-An-NDI-NH** (Figure 3c).



Figure 3. Fluorescence emission spectra of (a) Ph-NDI-NH, (b) 2-An-NDI-NH and (c) 9-An-NDI-NH in different solvents; A = 0.035, $\lambda_{ex} = 470$ nm; Optically matched solutions were used. 20 °C.

The quenched fluorescence of **Br-NDI-NH** ($\Phi_F = 23\%$) as compared to **Ph-NDI-NH** ($\Phi_F = 84\%$) can be rationalized by the heavy atom effect. It should be noted the fluorescence quantum yield of **2-An-NDI-NH** ($\Phi_F = 5.7\%$) and **9-An-NDI-NH** ($\Phi_F = 6.0\%$) are much lower than **Ph-NDI-NH**, the PET (anthryl moiety as the electron donor) is a possible reason for the fluorescence quenching.⁵¹ The results infer that although the coupling of the anthryl and NDI is not manifested in the UV–vis absorption spectra, the coupling indeed exerts significant effect on the excited state property, such as the fluorescence. It is known that the two coupling for the S₀ \rightarrow ¹CT (FC) and the for ¹CT* \rightarrow S₀ can be different.^{4,5}

The singlet oxygen quantum yields (Φ_{Δ}) of the compounds were determined (Table 2), as a preliminary evolution of the triplet state production ability of the compounds. For **Bis-Ph-NDI** ($\Phi_{\Delta} = 0\%$) and **Bis-2-An-NDI** ($\Phi_{\Delta} = 9.0\%$), the quantum yields are much lower than **NDI** ($\Phi_{\Delta} = 17\%$). These results indicate that CR in the dyes, both **Bis-Ph-NDI** and **Bis-2-An-NDI**, does not

produce triplet state efficiently. Thus the SOCT-ISC is not significant. Similar results were observed for 2-An-NDI-NH and 9-An-NDI-NH, *i.e.* the decay of the CSS of these dyads are mainly ${}^{1}\text{CT} \rightarrow S_{0}$, without any significant production of triplet state. Moreover, for 9-An-NDI-NH, even the anthryl moiety and NDI moiety with orthogonal conformation (Figure 9), the triplet quantum yield ($\Phi_{T} = 19\%$) is not high.

Table 1. The Absorption Properties, the Ground State Dipole Moments (μ_g), Transition Dipole Moments for the CT Absorption Bands (M_{abs}) and the Electronic Coupling Matrix Elements (V_{DA}) of the Compounds.

	$\lambda_{abs}{}^{a}(\epsilon^{b})$	$\mu_{\rm g}{}^c$ / D	$M_{ m abs}{}^d/ m D$	$V_{\rm DA}{}^{e}/{\rm eV}$
Bis-Ph-NDI	363 (1.3), 381 (1.6) ^{<i>f</i>} /421 (0.7) ^{<i>g</i>}	0	2.38	0.34
Bis-2-An-NDI	360 (2.4), 380 (2.2) ^{<i>f</i>} /533 (0.6) ^{<i>g</i>}	0	2.91	0.22
Br-NDI-NH	352 (0.80), 371 (0.90), 531(1.3) ^g	5.03	3.39	0.55
Ph-NDI-NH	351 (0.7), 371 (0.7) ^{<i>f</i>} /533 (1.2) ^{<i>g</i>}	2.83	3.27	0.40
2-An-NDI-NH	351 (1.2), 371 (1.1) ^{<i>f</i>} /533 (1.1) ^{<i>g</i>}	2.90	3.27	0.25
9-An-NDI-NH	371 (2.4), 390 (2.2) ^{<i>f</i>} /523 (1.1) ^{<i>g</i>}	3.05	2.94	0.36

 ${}^{a}c = 1.0 \times 10^{-5}$ M, in nm. ^{*b*} Molar absorption coefficient. ε , in 10⁴ M⁻¹ cm⁻¹. ^{*c*} The dipole moment of optimized ground state geometry at the B3LYP/6-31G(d)/level using Gaussian 09W, in Debye. ^{*d*} The transition dipole moment of S₀ \rightarrow ¹CT transition, in Debye. ^{*e*} The electronic coupling element matrix for electron transfer, in eV. ^{*f*} Absorption of S₀ \rightarrow ¹LE band. ^{*g*} Absorption of S₀ \rightarrow ¹CT band.

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	$\lambda_{abs}/nm^{a}(\epsilon^{b})$	λ_{em}/nm	$\tau_{\rm F}/{\rm ns}~^c$	$\Phi_{\mathrm{F}}(\%)^{d}$	$\tau_T(\mu s)$	$\Phi_{\Delta}(\%)^{e}$	$\Phi_{\mathrm{T}}(\%)^{f}$
NDI	363 (1.5), 381 (1.6) ^g	469	0.65	0.24	440	17 ^{<i>a</i>} , 58 ^{<i>h</i>} 86 ^{<i>i</i>}	j
Bis-Ph-NDI	363 (1.3), 381 (1.6) ^g /421 (0.7) ^k	_j	_ <i>j</i>	_ <i>j</i>	_ <i>j</i>	0 <i>a</i> , <i>h</i> , <i>i</i>	_j
Bis-2-An-NDI	360 (2.4), 380 (2.2) ^g /533 (0.6) ^k	_ <i>j</i>	_ <i>j</i>	_ <i>j</i>	1.6	9.0 ^{<i>a</i>} 0 ^{<i>h</i>, <i>i</i>}	_ l
Br-NDI-NH	352 (0.8), 371 (0.9) ^g /531(1.3) ^k	573	3.5	23	62	73 ^a 84 ^h 62 ⁱ	74
Ph-NDI-NH	351 (0.7), 371 (0.7) ^g /533 (1.2) ^k	573	10.4	84	161	20 ^{<i>a</i>} 16 ^{<i>h</i>} 13 ^{<i>i</i>}	42
2-An-NDI-NH	351 (1.2), 371 (1.1) ^g /533 (1.1) ^k	574	9.1	5.7	18	19 ^a 6.5 ^h 3.8 ⁱ	42
9-An-NDI-NH	371 (2.4), 390 (2.2) ^g /523 (1.1) ^k	568	9.6	6.0	22	13 ^a 5.0 ^h 2.8 ⁱ	19

^{*a*} In toluene, $c = 1.0 \times 10^{-5}$ M. ^{*b*} Molar absorption coefficient. $\varepsilon = 10^4$ M⁻¹ cm⁻¹. ^{*c*} Fluorescence lifetimes, biexponential fitting in toluene. ^{*d*} Fluorescence quantum yields. For **NDI**, anthracene in ethanol ($\Phi_F = 27\%$) as reference. For other compounds, diiodo-bodipy in CH₃CN ($\Phi_F = 2.7\%$) as reference. ^{*e*} Quantum yield of singlet oxygen (¹O₂). ^{*f*} The triplet quantum yields were obtained and 2,6-diio-dobodipy in toluene ($\Phi_T = 88\%$) as standard. $\lambda_{ex} = 532$ nm in toluene ^{*g*} Absorption of S₀ \rightarrow ¹LE band. ^{*h*} In DCM. ^{*i*} In CH₃CN. ^{*j*} Not applicable. ^{*k*} Absorption of S₀ \rightarrow ¹CT band. ^{*l*} Not determined.

3.3. Electrochemical Characterization and the Gibbs Free Energy Changes (ΔG_{CS}) of the Photo-induced Electron Transfer (PET) of the Dyads. The electrochemical properties of the NDI derivatives and reference compound anthracene were studied with cyclic voltammetry (Figure 4).⁴⁵



Figure 4. Cyclic voltammogram of the compounds. (a) anthracene (**An**), **NDI** and Ferrocene (Fc); (b) **Bis-Ph-NDI**, **Bis-2-An-NDI** and Fc; (c) **Ph-NDI-NH**, **Br-NDI-NH**, **2-An-NDI-NH**, **9-An-NDI-NH** and Fc. In deaerated DCM solutions containing 0.10 M Bu₄NPF₆ as supporting electrolyte and with Ag/AgNO₃ reference electrode. Fc was used as the internal reference, scan rates: 50 mV/s. 20 °C.

For NDI, an irreversible oxidation wave at ± 1.35 V was observed, as well as two reversible reduction waves at ± 1.09 V and ± 1.52 eV were observed (Figure 4a). One oxidation wave at ± 1.11 V for anthracene (An) was observed (Figure 4a). For **9-An-NDI-NH**, the first oxidation wave at ± 0.90 eV assigned to anthracene moiety and the first reduction wave at ± 1.32 eV assigned to NDI moiety were observed (Figure 4c), indicating that anthracene moiety acts as electron donor and the NDI unit as the electron acceptor in the PET process. Similar results were observed for NDI derivatives such as **Bis-2-An-NDI** and **2-An-NDI-NH** which are attached with anthracene moiety (Figure 4b and 4c). As for other NDI compounds attached with bromoor phenyl moiety, both an oxidation wave and the first reduction wave were according to NDI moiety. The electrochemical parameters of the compounds are presented in Table 3.

	An	NDI	Bis-Ph-	Bis-2-	Ph-NDI-	Br-NDI-	2-An-	9-An-
	All	ΠDΙ	NDI	An-NDI	NH	NH	NDI-NH	NDI-NH
$E(\mathrm{ox})(\mathrm{V})$	+1.11	+1.35	+1.35	+0.94	+1.37	+1.35	+0.93	+0.90
E(red)(V)	_	-1.09	-1.13	-1.08	-1.35	-1.26	-1.33	-1.32
		-1.52	-1.40	-1.49	-1.77	-1.66	-1.75	-1.77

Table 3. Redox Potentials of the Compounds ^a

^{*a*} Cyclic voltammetry in N_2 saturated DCM containing a 0.10 M Bu₄N[PF₆] supporting electrolyte; Counter electrode is Pt electrode; working electrode is glassy carbon electrode; Ag/AgNO₃ couple as the reference electrode.

The free energy changes of charge separation (ΔG_{CS}) can be calculated with the Weller equation (eqs 5 and 6).^{63–66} In the equations ΔG_S is the static Coulombic energy, e = electronic charge, E_{OX} = half-wave potential for one-electron oxidation of the electron-donor unit, E_{RED} = half-wave potential for one-electron reduction of the electron-acceptor unit, E_{00} = energy level approximated with normalized UV–vis absorption spectra and Fluorescence emission spectra, ε_S = static dielectric constant of the solvent, R_{CC} = center-to-center separation distance between the electron donor (Anthracene) and electron acceptor (NDI), determined by DFT optimization of the geometry, R_D is the radius of the electron donor, R_A is the radius of the electron acceptor, ε_{REF} is the static dielectric constant of the solvent used for the electrochemical studies, and ε_0 is the permittivity of free space. The solvents used in the calculation of free energy of the electron transfer are toluene (ε_S = 2.38), CH₂Cl₂ (ε_S = 8.93), MeOH (ε_S = 33.7) and acetonitrile (ε_S = 37.5). The free energy differences for the charge-separation (E_{CS}) were calculated with eqs 5 and 6. The data are collected in Table 4.

$$\Delta G_{\rm CS} = e[E_{OX} - E_{RED}] - E_{00} + \Delta G_{\rm S}$$
(Eq. 5)

$$\Delta G_{\rm S} = -\frac{e^2}{4\pi\varepsilon_{\rm S}\varepsilon_0 R_{\rm CC}} - \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{R_D} + \frac{1}{R_A}\right) \left(\frac{1}{\varepsilon_{\rm REF}} - \frac{1}{\varepsilon_S}\right)$$
(Eq. 6)

$$\Delta E_{\rm CS} = e[E_{OX} - E_{RED}] + \Delta G_{\rm S}$$
 (Eq. 7)

$$\Delta G_{\rm CR} = -(\Delta G_{\rm CR} + E_{00}) \tag{Eq. 8}$$

Table 4. Data of Gibbs Free Energy Changes of Charge Separation (ΔG_{CS}) and Energy Level of Charge Transfer States (E_{CTS}) of the Compounds in Different Solvents

		$\Delta G_{\rm C}$	cs (eV)				Ect	s (eV)	
	Tol	DCM	МеОН	ACN	Tol		DCM	MeOH	ACN
Bis-2-An-NDI ^a	-0.05	-0.60	-0.74	-0.75	+2.3	6	+1.81	+1.67	+1.66
2-An-NDI-NH ^b	+0.32	-0.22	-0.36	-0.37	+2.5	9	+2.05	+1.91	+1.90
9-An-NDI-NH ^c	+0.01	-0.31	-0.40	-0.40	+2.2	5	+1.93	+1.84	+1.84

^{*a*} $E_{00} = 2.41 \text{ eV}$. ^{*b*} $E_{00} = 2.27 \text{ eV}$. ^{*c*} $E_{00} = 2.24 \text{ eV}$. $E_{00} (E_{00} = 1240/\lambda)$ is the singlet state of NDI derivatives, λ is CT band absorption for **Bis-2-An-NDI**, but for **2-An-NDI-NH** and **9-An-NDI-NH**, λ is the wavelength of the crossing point of normalized UV–vis absorption spectra and Fluorescence emission spectra. "Tol" stands for toluene and "ACN" stands for CH₃CN.

It is clear that the CS is more favorable in polar solvents. PET of all three compounds is thermodynamically allowed in polar solvents, which was demonstrated by calculation of the Gibbs free energy changes using the Weller equation. PET is possible for 2-An-NDI-NH and 9-An-NDI-NH even in the non-polar solvent toluene. This result is in agreement with the fluorescence emission study of the compounds, showing a fluorescence quenching even in toluene in comparison with the reference compound Ph-NDI-NH, so determination error may

exist for the free energy changes of the charge separation. The energy level of the charge transfer state (CTS) was also calculated (Table 4). It was found that the CTS energy levels decrease in polar solvents as compared with that in non-polar solvents.

3.4. Nanosecond Transient Absorption Spectroscopy: The Triplet Excited States Properties of the Compounds. We studied the triplet states of the compounds by use of nanosecond transient absorption (ns TA) technique (Figure 5). For **Bis-2-An-NDI**, 532 nm radiation was used to selectively excite the CT absorption band. Excited state absorption (ESA) in the range of the 400–700 nm was observed. This ESA band is superimposed with the ground state bleaching band at 500 nm. The profile is similar to the T₁ state absorption of NDI moiety.^{61,67,68} The missing of the ground state bleaching band is due to the overlap with the ESA band, as well as the weak steady state absorption of **Bis-2-An-NDI** at 524 nm ($\varepsilon = 6900 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure 5a).



Figure 5. Nanosecond transient absorption spectra of (a) Bis-2-An-NDI ($\lambda_{ex} = 532$ nm), (b) Decay trace of Bis-2-An-NDI at 440 nm. $c = 4.0 \times 10^{-5}$ M in deaerated toluene. 25 °C.

The lifetime of triplet state was determined as 1.6 μ s (Figure 5b). This lifetime is much shorter than the previously reported triplet state of amino-substituted NDI chromophore (30 μ s),^{61,67,68} as

well as that of **Br-NDI-NH** (62 μ s). However, it is close to the T₁ state lifetime of the unsubstituted NDI (2.5 μ s in CH₃CN).⁵⁸ Moreover, the transient signal was totally quenched in aerated solution, indicating that the transient observed is due to the triplet excited state (Supporting information, Figure S33).

It is known that unsubstituted NDI shows efficient ISC via the $S_1 (\pi-\pi^*) \rightarrow T_4 (n-\pi^*)$ transition.⁵⁸ However, we carried out the excitation at 532 nm for **Bis-2-An-NDI**, which is selectively excited into the CT band, yet T_1 state was observed. This result indicates the ISC is from the ¹CT state, not the SO-ISC of An or NDI moieties, and the ISC mechanism should be SOCT-ISC.²⁸⁻³⁴ Other ISC channels, such as HFI, or mixing of the S_1/T_0 or $S_1/T_{\pm 1}$ sates, are unlikely due to the large *J* values of this compact electron donor/acceptor dyad.

The ns TA spectra of the amino-NDI compounds were also recorded (Figure 6 and Supporting information, Figure S29–32). For **Br-NDI-NH**, the typical T₁ absorption feature of the NDI moiety was observed upon photoexcitation (Figure 6a). The ground state bleaching band is overlapped with the ESA band in the range of 400 – 700 nm. Similar results were observed for the non-brominated NDI derivatives (Supporting information, Figure S30–32). The triplet state lifetimes observed for the amino-NDI compounds are in the range of 18 – 161 μ s (Table 2). These values ($\tau_T = 18 \ \mu$ s for **2-An-NDI-NH** or 22 μ s for **9-An-NDI-NH**) are close to the previously reported T₁ state lifetimes of amino-NDI moieties (32 μ s).⁶¹ These results show that the T₁ state of the dyads is the NDI-localized LE state, not the ³CT state.⁵ Previously an electron donor/acceptor triad based on NDI was shown to be with RP-ISC, and the electron exchange was studied with time-resolved EPR spectra, but the triplet state of Bodipy was produced in C₆₀-Bodipy dyads by charge recombination in non-polar solvents, such as toluene, but not in polar

dependent ISC. 0.18 .0.12 0 0 0.06 0.00 Wavelength / nm 0.09 0.06 0 0 0.03 0.00

solvent of acetonitrile.^{63,64} Dyads Bis-2-An-NDI and Bis-Ph-NDI show similar solvent-

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0 µs

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b

 $\tau = 62 \ \mu s$

Time / µs

τ = 22 μs

d



3.5. Femtosecond Transient Absorption Spectroscopy. The ISC of NDI and Br-NDI-NH has already been reported,⁵³ however, the excited-state dynamics of anthracene substituted NDI derivatives was rarely studied. In this donor-acceptor system, anthracene moiety acts as electron donor and NDI moiety as electron acceptor. Hence, the forming triplet state may undergo the charge separation and charge recombination pathway, known as SOCT-ISC. To study the



kinetics of the above two processes, the $S_0 \rightarrow S_1$ band at 340 nm instead of $S_0 \rightarrow {}^1CT$ was excited in femtosecond transient absorption (fs TA) studies (Figure 7).



Figure 7. (a) Femtosecond transient absorption spectra of 9-An-NDI-NH in toluene, (b) Corresponding species-associated difference spectra (SADS) obtained from target analysis and (c), (d) Kinetic traces at selected wavelengths, $\lambda_{ex} = 340$ nm, 20 °C.

Upon excitation at 340 nm in toluene, **9-An-NDI-NH** exhibits a broad ESA band in the range 350 - 750 nm, which is attributed to $S_1 \rightarrow S_n$ absorption, with a "valley" between 500 and 525 nm as a result of overlap with ground state bleaching (GSB) band. The ESA band at 450 nm decays with $\tau = 820$ fs (Figure 7c). Meanwhile, one broad band between 350 to 530 nm centered at 460 nm and another broad band centered at 600 nm (the ESA band of NDI^{-•}) develop with the same time scale (Figure 7a), indicating the formation of a CS state.⁶⁹⁻⁷¹ The biexponential decay

of ESA at 710 nm of An^{+•} was obtained, though this band was buried by the ESA of NDI^{-•} (Figure 7d).⁷² Subsequently, on an 50 ps time scale, both of two positive features decay and show blue-shift, indicating the occurrence of charge recombination (CR). Both of 420 and 580 nm bands can be assigned to triplet state absorption since they did not decay totally on the time scale of our measurements (1 ns).

We have made the target analysis of our transient absorption spectra (Glotaran software) and assumed that three states, the S₁ state, the CSS due to NDI^{-•}and An^{+•}, T₁ state of **9-An-NDI-NH**, are involved. We have applied the sequential model, thus the species-associated decay spectra (SADS) of each state and the rate constants are obtained. In CH₃CN, the decay of S₁ state (710 fs) is slightly faster than that in toluene (850 fs), indicating faster electron transfer in CH₃CN (Supporting information, Figure S34). The rate constant of CR in CH₃CN is 18 ps, which is also faster than that in toluene (50 ps). Considering the close proximity of CSS in toluene (2.25 eV) and T₄ state (2.18 eV). Thus the CR in toluene is probably in Marcus inverted region.^{4,5,73} (Scheme 2).

The rate constants of CS and CR of **2-An-NDI** are 0.22 ps and 17 ps, respectively (Supporting Information, Figure S35). The rate constants of CS and CR of **Bis-2-An-NDI** are also presented (Supporting Information, Figure S36).

3.6. Fluorescence Up-conversion Spectroscopy. In order to further study the decay of the CT state, femtosecond fluorescence spectroscopy was applied (Figure 8 and Figure S37 from Supporting information) show the femtosecond fluorescence data for **9-An-NDI-NH** at $\lambda_{ex} = 400$ nm and $\lambda_{em} = 550 - 610$ nm. Two decay time components are obtained.

The time scale of the first decay component is 0.80 - 3.4 ps, which is attributed to vibrational relaxation. The amplitude of this time component becomes smaller at longer emission

wavelengths. The time scale of the second decay component is 47 - 71 ps. We attributed it to charge recombination process, which is demonstrated by femtosecond transient absorption spectrum (Figure 7b). The percentage of the component resulting from fitting of fluorescence kinetics is also given in Figure 8 and Supporting information (Figure S37).



Figure 8. Fluorescence decay of **9-An-NDI-NH** in toluene at 570 nm. Determined with the fluorescence upconversion method.

3.7. DFT Calculations. The ground state geometries of the compounds were optimized (Figure 9). For the dyads containing amino substituent, the dihedral angles between the amino moiety and the NDI is 0 °, thus full conjugation between the amino-nitrogen atom p-orbital and the NDI π -framework is expected.¹ This postulation is in agreement with the strong electronic coupling and the thus the appearance of the strong CT band in the absorption spectra of the compounds (Figure 1).

For **Bis-Ph-NDI**, the dihedral angles between the phenyl moiety and the NDI unit is 62° , slightly larger than the dihedral in **Bis-2-An-NDI** (57°), moreover, the electron donating of phenyl moiety (HOMO energy level is -6.69 eV. Table 5) is weaker than anthryl (HOMO

 energy level is -5.47 eV. Table 5).⁵² All above features are unfavorable for electronic coupling. For **2-An-NDI-NH** and **9-An-NDI-NH**, the dihedral angles between the anthryl moiety and the NDI unit is 61° and 88°, respectively. As the substitution is at different position of anthracene, The large difference of these two dihedral angles is due to that **9-An-NDI-NH** has a larger steric hindrance compared with **2-An-NDI-NH**.



Figure 9. Optimized ground state (S₀ state) geometries of (a) **Br-NDI-NH**, (b) **Bis-Ph-NDI**, (c) **Bis-2-An-NDI**, (d) **Ph-NDI-NH**, (e) **2-An-NDI-NH** and (f) **9-An-NDI-NH**, calculated by DFT//B3LYP/6-311G(d, p) level with Gaussian 09W. The dihedral angles of the aryl moiety and NDI moiety, the amino moiety and NDI moiety are also presented.

It should be noted that with the full π -conjugation between the amino-moiety and the NDI moiety, the coupling of the anthryl in **2-An-NDI-NH** and **9-An-NDI-NH** does not contribute to the CT absorption bands (Figure 1). Although they do induce distinct CT absorption band in **Bis-2-An-NDI**, *i.e.* no add-up or synergic effect was observed for the electronic coupling.

The steric hindrance encountered about the rotation of the C–C linker of the phenyl/anthryl moiety and NDI was studied in detail by construction of the potential energy curve (Figure 10). For **Bis-Ph-NDI**, **Bis-2-An-NDI**, **Ph-NDI-NH** and **2-An-NDI-NH**, the potential energy curves is flat, (< 0.05 eV for conformation with dihedral angle of 60° ~120°). For **9-An-NDI-NH**, however, the potential energy curve is steep.



Figure 10. Potential energy surfaces of the ground state of of (a) **Bis-Ph-NDI**, **Bis-2-An-NDI**, **Ph-NDI-NH**, **2-An-NDI-NH** and **9-An-NDI-NH**, calculated at the DFT//B3LYP/6-311G(d, p) level with Gaussian 09W. The dihedral angle refers to the aryl moiety with respect to the NDI scaffold; (b) the magnified low energy range of (a).

The frontier molecular orbitals of the compounds were presented (Table 5). With attachment of either the amino moiety, phenyl or the anthryl moiety, the energy level of HOMO increased significantly, and at the same time, the energy level of the LUMO decreased significantly as compared to that of **NDI**. For the anthryl derivatives, the MOs (Molecular orbitals) are basically confined on either the anthryl or the NDI moiety for HOMO and LUMO, respectively, but delocalization does exist for MOs of HOMO–1 and LUMO+1. In comparison, the delocalization

between the NDI and amino moiety is more significant, the delocalization is necessary for electronic coupling.

Table 5. Selected Frontier Molecular Orbitals and Energy Level (eV) of the Compounds, calculated at DFT//B3LYP/6-311G (d, p) Level with Gaussian 09W.

	HOMO – 1	HOMO	LUMO	LUMO + 1
NDI			, *** *	
	− 7.25 eV	●●● -3.61 eV	–1.88 eV	–1.52 eV
Bis-Ph-NDI	89 C.	881		-
	–6.88 eV	–6.69 eV	-3.48 eV	–1.80 eV
Bis-2-An-NDI	.		and a state of	
	5 60 eV	5 57 eV	3.51.eV	2 05 eV
Ph-NDI-NH	-3.00 ev	-3.37 67	-3.31 ev	-2.03 ev
			- `\$0€}0 • ₹`}@ *±≈;. ~,	·*************************************
	-6.74 eV	-6.14 eV	–3.23 eV	–1.64 eV
BL-NDI-NH			· · · · · ·	
	–7.04 eV	–6.11 eV	–3.20 eV	_1.49 eV
2-An-NDI-NH	3000 Frank	· · · · · · · · · · · · · · · · · · ·		
	–6.16 eV	–5.45 eV	–3.27 eV	–1.91 eV
9-An-NDI-NH		، بر من من م		ురి. 6 చి. ఈ పి.చి. చి. గారాలు సంగ
	-6.22 eV	●● -5.38 eV	–3.24 eV	–1.88 eV

Scheme 2. Simplified Jablonski Diagram Illustrating the Photophysical Processes with (a)





^{*a*} Key words: The energy levels of singlet state origin from LE state absorption, the energy level of charge separated state comes from electrochemical parameters and that of triplet state were obtained at TDDFT//B3LYP/6-311G(d, p) level with Gaussian 09W, based on the optimized excited state geometries. "An" stands for anthracene, "NDI" stands for naphthalenediimide, "Tol" stands for toluene and "ACN" stands for CH₃CN.

The photophysical processes are summarized in Scheme 2. For **9-An-NDI-NH**, triplet production in toluene ($\Phi_{\Delta} = 13\%$) is higher than that in acetonitrile ($\Phi_{\Delta} = 2.8\%$). The reason is that the CSS in toluene (2.25 eV) is close to T₄ state (2.18 eV), which is localized on NDI. Thus the SOCT-ISC is facilitated. The CSS lifetime in toluene is 50 ps, whereas the CSS lifetime in acetonitrile 18 ps. Thus the CR in toluene is probably in Marcus inverted region.^{4,5,73} In acetonitrile, however, the CSS is with much lower energy. It is probably still on the top of the parabola of the Marcus $k_{\text{ET}} \sim \Delta G_{\text{CT}}$ curve, *i.e.* the CR is with faster kinetics, which competes with ISC, thus the Φ_{T} in acetonitrile is lower. This is a general trend for the dyads/triads studied here. Similar results were observed for the molecular systems for which the ISC is based on

charge recombination.^{63,64} RP-ISC mechanism is unlikely, due to the large coupling in these compact electron donor/acceptor dyads.^{27,74,75}

Low ISC yield was observed for the anthracene-NDI dyads. The exact reason for this result is unclear. There are two possible reasons. One is the matching of the CT state and the triplet state energy levels, perhaps in the cases the matching is un-optimal. The second reason may be the mutual orientation of the NDI and the anthracene planes. For **Bis-2-An-NDI** and **2-An-NDI-NH**, the dihedral angle between the NDI and the anthryl moieties are 57 ° or 61 °, which are not beneficial for SOCT-ISC (which requires orthogonal orientation between the electron donor and acceptor, 90 °).^{31,32} Moreover, for **9-An-NDI-NH**, although the NDI and the anthryl moieties are not in orthogonal geometry, yet the axes, or the dipole moments, of the two moieties are not in orthogonal orientation, and it is clearly different from the orthogonal geometry of the reported Bodipy-anthracene dyads which show highly efficient ISC.³² All these factors may contribute to the low ISC yield of the NDI-An dyads or the triad.

3.8. Conclusion. We attached different electron donors of phenyl, anthryl or amino moiety, to naphthalenediimide (NDI), an electron acceptor. The purpose is to study the effect of electronic coupling (the magnitude is the matrix element, V_{DA}) between the donor and acceptor on the photophysical properties of the compact electron donor/acceptor dyads, such as UV–vis absorption, fluorescence emission and intersystem crossing. We found the V_{DA} is dependent on the electron donating strength of the aryl moieties, as well as the molecular conformation. Weaker electron donating moiety (amino moiety) shows a larger electron coupling matrix element ($V_{DA} = 0.55$ eV, $\varepsilon = 1.3 \times 10^4$ M⁻¹ cm⁻¹ for CT band), due to the π -conjugation of the amine with NDI moiety. Accordingly, stronger electron donating moiety (anthryl moiety) for **9**-**An-NDI-NH** shows a smaller electron coupling matrix element ($V_{DA} = 0.36$ eV, $\varepsilon = 1.1 \times 10^4$

 M^{-1} cm⁻¹ for CT band). CT absorption bands with different magnitude were observed in UV–vis absorption spectra. Based on steady-state and femtosecond/nanosecond transient absorption spectroscopies, the photo-induced charge separation (0.83 ps) and charge recombination (50 ps) lifetimes of **9-An-NDI-NH** were determined, these two processes for **2-An-NDI-NH** are 0.22 ps and 17 ps. We found that electron coupling does not show the add-up effect, *i.e.* with attachment of an amino moiety, inducing an extra anthryl moiety does not increase the magnitude of the CT absorption band, although there is a strong electronic coupling between the anthryl moiety and NDI moiety in a reference compound. Solvent polarity-dependent ISC was observed for the dyad/triads because the singlet oxygen quantum yield (Φ_{Δ}) decreases in solvents with high polarity, the CR induced ISC is with efficiency in the range of 19 ~ 42%, and the lowest triplet state (³LE) is localized on NDI, not a ³CT state. This result indicates that orthogonal geometry does not lead to efficient charge recombination induced ISC.

ASSOCIATED CONTENT

S Supporting Information

NMR and HR-MS spectra, steady state UV–vis absorption and luminescence spectra, nanosecond transient absorption spectra and DFT/TDDFT calculation details about other compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI:

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TOC Graphic

