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Polymeric Near Infrared Emitters with Bay-Annulated Indigo Moieties

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Three new copolymers based on bay-annulated indigo (BAI) building blocks were synthesized through Stille-type cross-coupling reactions, alternating the electron-deficient BAI units with thiophene-based donor moieties. Those polymers showed absorption and fluorescence emission in the NIR region. Their spatial structures were found to prevent aggregation-caused quenching (ACQ) in the solid state. Photoluminescence at 77 K is found ca. four times more intense than at 293 K. Based on time-resolved photoluminescence experiments, the excited-state energy transfer hopping deactivation in the copolymers is discussed in terms of a Förster-type mechanism, with time constants ranging from $10^{10}$ to $10^{11}$ s$^{-1}$.

Introduction

Natural dyes and pigments as indigo (Scheme 1) and its natural (indigoids) or synthetic derivatives are valued for their bright color and high photochemical stability and have been used since antiquity.\(^1\)\(^{-5}\) A bay-annulated indigo derivative known as Cibalackrot (7,14-diphenyldiindolo[3,2,1-de; 3′,2′,1′-ij][1,5]naphthyridine-6,13-dione), an industrial dye that has been known for over a century,\(^6\) has a highly rigid chemical structure, showing strong luminescence\(^7\) and is, as indigo, capable of singlet fission\(^8\)\(^,\)\(^9\) and can be used as an organic laser dye.\(^10\)

The need for better performing and stable organic materials in organic electronics inspired the resurgence of historically long known molecules as indigo\(^11\)\(^,\)\(^12\) and their subsequent chemical transformation into new families of $\pi$-conjugated building blocks\(^12\), also for construction of new macromolecular semiconductors.\(^11\) In this work, indigo was functionalized by reaction with 2-thienylacetyl chloride, as described previously\(^13\)\(^,\)\(^14\), to produce the bay-annulated indigo derivative BAI1 (Scheme 1). The electron-deficient BAI1 moiety is a suitable building block for the generation of push–pull type conjugated polymers.\(^15\) In recent years copolymers comprising these building blocks have been studied for their suitability in OFETs and OPVs applications.\(^13\) Moreover, these donor-acceptor copolymers are also attractive in view of a potential application in organic solar cells\(^16\) and as NIR detectors. More specifically, near-infrared photodetection (NIR-OPD, @800-3000 nm)\(^17\) is valuable for numerous scientific as well as industrial (inspection, sorting, safety/security) and recreational applications. Nowadays, near-infrared photodetectors are commonly based on inorganic semiconductors such as InGaAs, InGaSb\(^18\) or HgCdTe\(^19\), although organic-based NIR detectors,\(^18\)\(^,\)\(^20\)\(^-\)\(^24\) have gained increasing interest. To date, a very limited amount of well performing NIR-OPDs have been reported\(^24\). Recently, push–pull copolymers based on BAI indigo core were found to have a suitable for photodetection beyond 1000 nm.\(^19\)

![Scheme 1. Structures and acronyms of indigo and its bay-annulated derivates, Cibalackrot and BAI1, together with the chemical structures of the thiophene-based building blocks (C$_2$CPDT and BDT) used to prepare the NIR-emitting copolymers: PBAIC-1, PBAIC-2 and PBAIBD-1.](image-url)
Here, we investigate the ground- and excited-state characteristics of copolymers comprising BAII units, linked through thiophene-based donor units (cyclopentadithiophene CPDT- or benzodithiophene BDT-based) to verify the potential of such copolymers as NIR solid state emitters. A rational design of the polymers indicates that the introduction of planarized and symmetrical thiophene donors (CPDT, 4H-cyclopenta[1,2-b:5,4-b’]dithiophene, and BDT, benzo[1,2-b:4,5-b’]dithiophene) should enable interchain π-π stacking and maximized on-chain electronic interaction, thus promoting the bulk charge transport. Furthermore, the donor blocks, of the donor-acceptor copolymers, have been structurally varied to evaluate their influence on its electronic properties. Additionally and since the BAII acceptor units do not carry solubilizing side chains, the donor blocks have been also used to induce a sufficient solubility.

**Experimental Section**

**Materials**

Reagents were purchased from Sigma-Aldrich, Fischer Scientific or TCI and used without further purification, unless otherwise indicated. For the photophysical studies, the solutions were prepared with solvents of spectroscopic grade or equivalent: 2-methyltetrahydrofuran (2-MeTHF, Anhydrous/Inhibitor free, Sigma-Aldrich), tolune (tol, 99+% for spectroscopy, Acros Organics) and analytical grade Chloroform (Fischer Chemical). Silver nitrate (AgNO₃, for analysis, Panreac), Ferrocene (for synthesis, Merck) and tetrabutylammonium hexafluorophosphate (NBu₄PF₆, ≥99.0% for electrochemical analysis, Sigma-Aldrich) were used in cyclic voltammetry assays without further purification. BAII was obtained from double annulation of indigo as described in Scheme1; 4,8-Bis((2-butyloctyl)oxy)benzo[1,2-b:5,4-b’]dithiophene (C₁₂CPDT) was synthesized as previously described. 4,8-Bis((2-butyloctyl)oxy)benzo[1,2-b:4,5-b’]dithiophene (BDT) was obtained from TCI and used without further purification.

**Thin films preparation**

Polymer thin films were obtained with a desktop precision spin-coating system, model P6700 series from Speedline Technologies, as described elsewhere. Solutions for spin-coating were prepared by adding 2 mg of the polymers to 200 μL of chloroform solution, with stirring in the dark, at room temperature, overnight. Thin films from the samples were obtained by deposition of ca. 50 μL from a solution of the compounds into a circular sapphire substrate (10 mm diameter) followed by spin-coating (2500 rpm) in a nitrogen-saturated atmosphere (2 psi).

**Photophysical and electrochemical studies**

Absorption and fluorescence spectra were recorded on Agilent Cary 5000 UV-Vis-NIR and Horiba-Jobin-Ivon SPEX Fluorolog 3-22 spectrometers respectively. Absorption spectra of the transparent thin films were obtained in absorption mode using a clean sapphire substrate as the reference sample. The fluorescence spectra were corrected for the wavelength response of the system. For the steady state and time resolved emission experiments, the absorption at the excitation wavelength was kept below 0.1 values to avoid aggregation effects. Acquisition of the photoluminescence spectra of the polymers at NIR were performed with Hamamatsu R5509-42 photomultiplier, cooled to 193 K in a liquid nitrogen chamber (Products for Research model PC176TSC-005), connected to the fluorimeter. The colour parameters were determined according to the CIE (Commission Internationale de l’Eclairage proceedings) 1931 scale diagram. The x and y colour parameters were determined with the acquisition of the transmittance spectra using Shimadzu UV-2600 equipped with Colour Analysis software.

Fluorescence quantum yields (φ) of the polymers in solution were determined with three replicates, by William’s method, using indocyanine green (IR-125 in ethanol, φ= 0.132) as standard. The φ of the model monomers in solution were measured using the absolute method with a Hamamatsu Quantaurus QY absolute photoluminescence quantum yield spectrometer, model C11347 (integration sphere). The φ of the polymers in thin films were measured by the absolute method with an integrating sphere module, as described elsewhere. The following equation was used to determine the φ of the BAII polymers thin films:

\[
\phi_{S}(\text{solid}) = \frac{\int_{\lambda_{\text{sample}}}^{\lambda_{\text{sample}}+\Delta\lambda} I_{\text{sample}}(\lambda) d\lambda - \int_{\lambda_{\text{sample}}}^{\lambda_{\text{sample}}+\Delta\lambda} I_{\text{scattered}}(\lambda) d\lambda}{\int_{\lambda_{\text{sample}}}^{\lambda_{\text{sample}}+\Delta\lambda} I_{\text{scattered}}(\lambda) d\lambda}
\]

where \( \phi_{S} \) (solid) is the fluorescence quantum yield of polymer thin film, \( \int_{\lambda_{\text{sample}}}^{\lambda_{\text{sample}}+\Delta\lambda} I_{\text{sample}}(\lambda) d\lambda \) is the integrated area under the emission of the polymer thin film (which excludes the integration of the Rayleigh peak), \( \int_{\lambda_{\text{sample}}}^{\lambda_{\text{sample}}+\Delta\lambda} I_{\text{scattered}}(\lambda) d\lambda \) is the integrated area under the Rayleigh peak of a sample containing only a clean sapphire support, and \( \int_{\lambda_{\text{sample}}}^{\lambda_{\text{sample}}+\Delta\lambda} I_{\text{scattered}}(\lambda) d\lambda \) is the integrated area under the Rayleigh peak in the emission spectra of polymer in thin film.

Fluorescence decays were measured using a home-built picosecond time-correlated single photon counting (ps-TCSPC) apparatus described elsewhere. Excitation was performed with the second harmonic, 372 nm or 402 nm (generated with a Spectra Physics GWU-23PS module) from a picosecond Spectra Physics mode-lock Tsunami laser (Ti:Sapphire) model 3950 (80 MHz repetition rate, tuning range 700-1000 nm), pumped by a Millennia Pro-10s, continuous wave, solid-state laser (532 nm). The fluorescence decays and the instrumental response function (IRF) were collected using 1024 channels in a time scale up to 24.4 ps/channel (using a Spectra Physics frequency divider, Pulse picker model 3980-2s, to reduce the fundamental laser repetition rate). Deconvolution of the fluorescence decay curves was performed using modulation function method, as implemented by G. Striker in the SAND program, and previously reported in the literature. The time resolved ultrafast transient absorption measurements were collected in a broadband HELIOS spectrometer (350–1600 nm) from Ultrafast Systems as elsewhere described. The transient absorption data was obtained with excitation at 420
Electrochemical cell of capacity 5 mL. A glassy carbon electrode (GCE) (d = 3 mm) was the working electrode, glassy carbon (GC) was performed using Glotaran software. Hexafluorophosphate, (d = 1.6 mm) wire the counter electrode and Ag/Ag+ vs. NBu₄PF₆, in 0.1 M tetrabutylammonium hexafluorophosphate, NBu₄PF₆, in MeCN as the reference electrode. Ferrocene/ferrocenium (Fc/FC₃) redox couple were used as the internal reference. The reference and polymers were dissolved in 0.1 M NBu₄PF₆ in CHCl₃ solution to acquire cyclic voltammograms with a 50 mV/s scan rate with a window potential between −1.6V to 1.0 V (vs. Ag/Ag+).

Results and Discussion
Synthesis and characterization
The general scheme for the synthesis of the monomeric BAI precursors BAI2 and BAI4 is depicted in Scheme 2. For the synthesis of 7,14-di(thiophen-2-yl)diindolo[3,2,1-de:3',2',1'-ij][1,5]naphthyridine-6,13-dione (BAI1) indigo is first subjected to a double annulation reaction to form the BAI core. Hereby, an twofold amidation followed by an intramolecular aldol condensation takes place. In the second step, the 2-positions of the thiophene rings are brominated to form 7,14-bis(5-bromothiophen-2-yl)diindolo[3,2,1-de:3',2',1'-ij][1,5]naphthyridine-6,13-dione (BAI2). An subsequent Stille-type coupling reaction, catalyzed by tetrakis(triphenylphosphane)palladium(0) as catalyst and tri(o-tolylphosphane) as ligand together with the monomers BD5 and BAI2 was dissolved in toluene and heated to 100°C. After six days, the copolymer was precipitated and Soxhlet extracted (Scheme 3).

Scheme 2. Synthesis of BAI monomers. Reaction conditions: (i) 2-thienylacetyl chloride, xylene, 145ºC, 48 h, 38.5%; (ii) NBS, chloroform, rt, 15h, 69.7%; (iii) 2-(trimethylstannyl)-3-dodecylthiophene, Pd(PPh₃)₄, Ph3-tol, toluene, 100ºC, 4 days, 1.5%; (iv) NBS, chloroform, rt, 12h, 87.1%.

The Stille-type cross-coupling reaction of the two different BAI monomers (BAI2 and BAI4) with distannyldi(CPD)T(4,4-bis(2-octyldodecyl)-2,6-bis(trimethylstannyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diy1, CPDT) was carried out as previously described for the synthesis of corresponding indigo-containing copolymers.

Hereby, tetrakis(triphenylphosphane)palladium(0), Pd(PPh₃)₄, was used as catalyst in a microwave-assisted coupling reaction. After irradiation at 125°C for 25 minutes, the reaction mixture was stirred at 90°C for further 72 h (Scheme 3). The copolymers PBAIC-1 and PBAIC-2 were precipitated into cold methanol and fractionated by Soxhlet extraction. For the synthesis of the BAI-benzodithiophene copolymer PBAIBD-1, the reaction conditions were modified according to a report by He et al., Under inert conditions, pris(dibenzyldieneacetone)dipalladium(0) as catalyst and tr(o-tolylphosphane) as ligand together with the monomers BD5 and BAI2 was dissolved in toluene and heated to 100°C. After six days, the copolymer was precipitated and Soxhlet extracted (Scheme 3).

Scheme 3. General synthetic scheme for the generation of the BAI-based copolymers: PBAIC-1, PBAIC-2 and PBAIBD-1.

PBAIC-1 and PBAIBD-1 show moderate molecular weights $M_n$ of 8-11k g·mol⁻¹, with PD = 1.33 and 1.39, respectively, resulting possibly from a limited solubility of the products. The two
additional dodecylthiophene moieties in copolymer PBAIC-2 increase the solubility of the polymer, thus probably causing its higher molecular weight and polydispersity ($M_n = 11-23 \text{ kgmol}^{-1}$, PD = 1.94). Nevertheless, with a value below 2, the PDI index is still as expected for polycondensations. For further synthetic procedure and structural characterization, please consult the supplementary material.

Optical and electrochemical properties

The photophysical properties of the three BAI copolymers were investigated in solution (2-MeTHF and toluene) and in thin films and compared to their monomeric units. In Figure 1, the absorption and emission spectra of PBAIC-1 and PBAIC-2 in 2-MeTHF solution are compared with BAI1 and CPDT. PBAIC-1 is compared to BAI1 and BDT. The change of the phenyl groups of Cibalackrot to the electron-richer thiophene groups in BAI1 lead to a bathochromic shift of the absorption maximum of ~40 nm: 547 nm for Cibalackrot to 588 nm for BAI1 (Figure S14; Table S12). Generally, incorporation of the BAI chromophores into the copolymers causes a significant red shift of the absorption and emission of these in comparison to BAI1.

The shape of the absorption spectra is found similar for the three copolymers, with two broad absorption bands: one (I) in the 300-500 nm region and (II), broader, at 550-1000 nm. The bathochromic shift of band I of the copolymers (PBAIC-1, PBAIC-2 and PBAIBD-2) that may be assigned to the donor units, in comparison to the absorption bands of the monomeric donor chromophores (BDT and CPDT), may indicate the conjugative interaction between the subunits. The interplay of first and second absorption band of the copolymers causes a green color of the copolymers, in contrast to the purple color characteristic of BAI1 (Figure 1). The red shift of the second (II) absorption band in comparison with BAI1 can be associated to an extended $\pi$-conjugation and a strong donor-acceptor character of the copolymers. PBAIC-1 and PBAIC-2 (with the CPDT moiety as electron donor unit) in 2-MeTHF solution display emission spectra with bands in the 800-1200 nm region, with peak maxima at 997 and 982 nm, respectively, while PBAIBD-1 shows an emission spectrum with two peaks: 778 nm (visible region) and 944 nm (NIR), see Table 1. The electronic spectra of the three copolymers in toluene (Figure S15) are almost identical to the spectra in 2-MeTHF solutions (see Table S13). The introduction of the donor CPDT unit (from PBAIC-1), instead of BDT (PBAIBD-1), leads to a red-shift of the absorption either in solution, or in solid state. Nonetheless, solid state absorption bands are red-shifted relative to the solution spectra (Figure S15). Fluorescence quantum yields ($\phi_f$) of the BAI-containing copolymers obtained in 2-MeTHF, at 298 K and 77 K, and in thin films at 298 K (Table 1) are roughly similar to the solid state (thin films) values. The spatial structure of PBAIC-1, PBAIC-2 and PBAIBD-1 as donor-acceptor copolymers seems to preclude aggregation caused quenching (ACQ) effects. Moreover, the $\phi_f$ values of the BAI copolymers at 77 K are about four times higher than in solution at 293 K (see Figure S16 and Table S14), as factor of interest for potential applications, e.g. as photoactive layer of NIR organic photodiodes. The PL emission area of the three polymers presented a linear course with the increase of the absorption at the excitation wavelength, in solution (Figure S17), ruling out aggregation effects of the polymer in 2-meTHF.

The electrochemical properties and energy levels of BAI copolymers were determined in chloroform solution (Table 2). The characteristic double reduction the amide groups, correlated to the BAI moiety, quasi-reversible, is prominent in cyclic voltammogram of PBAIBD-1. Moreover, the oxidation and reduction potentials are similar to those found in the literature to D-A type polymers based on Bay-annulated indigo and thiophene.\(^{13, 16, 19}\) The energies of the HOMO and LUMO levels were obtained according to equations (2) and (3).\(^{30}\)

$$E_{HOMO} = -\left(E_0^{\text{ox}} + 4.8\right) - E_{FOC}$$

$$E_{LUMO} = E_{HOMO} + E_0 - 0$$

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The energy of the HOMO, \( E_{\text{HOMO}} \), was calculated from the onset oxidation potential, \( E_{\text{onset}}^\text{ox} \), plus 4.8, which is the reference energy level of ferrocene below the vacuum level and the oxidation potential of ferrocene, \( E_{\text{FOC}} \), given by the potential of FOC/FOC' vs Ag/Ag+ measured by cyclic voltammetry in solution (Figure 2). The LUMO energy, \( E_{\text{LUMO}} \), was obtained from the optical energy gap \( E_{\text{gap}} \) measured from the interception of the normalized UV-Vis absorption and fluorescence spectra, through equation (3).

The HOMO-levels of the CPDT-based polymers are similar with values of -4.96 eV (PBAIC-1) and -4.95 eV (PBAIC-2), respectively, and correlate well with values determined from the onset of absorption (Table S1). The LUMO-levels, about -3.5-3.9 eV, is closely correlated to the \( E_{\text{LUMO}} \) = -3.6 eV, previously attributed to the model compound BAI. CPDT-based polymers also presented smaller band gaps than PBAIBD-1 (built with BDT as donor unit), thus, CPDT may be a a stronger electron donor unit than BDT and therefore gives higher HOMO energy levels (Table 2).

The band gap energies of BAI copolymers vary between 1.3-1.5 eV, when determined either by CV, or UV-spectroscopy (Table 2). Narrow band gap ( Eg ) conjugated polymers, 1.1 ≤ Eg ≤ 2.1 eV, have especially low lying LUMO energies making them excellent candidates for n-type OFET materials. Moreover, these BAI copolymers also display optical absorption in the near-IR region of the electromagnetic spectrum, ideal for OPV devices. Also, because these polymers contain both donor-acceptor moieties on their single main backbones, they are promising candidates for replacing polymer blends used as active layers in manufacturing all polymeric solar cells, and thus, overcome drawbacks such as miscibility between the donor and acceptor polymer and gradual phase separation of polymer blend films.

### Table 1. Room temperature spectroscopic data (absorption and fluorescence emission maxima together with Stokes shift, \( \Delta \lambda \)) and fluorescence quantum yield (\( \Phi_F \)) for the BAI copolymers and model monomers at T= 298 K.

| Compound | Medium | \( \lambda_{\text{em}} \) (nm) | \( \lambda_{\text{em}} \) (nm) | \( \Delta \lambda \) (cm\(^{-1}\)) | \( \Phi_F \) |
|----------|--------|-----------------|-----------------|----------------|---------|
| C6CPDT   | 2-meth | 316             | 363             | 4097           | 0.048\(^*\) |
| BDT      | 2-meth | 351             | 385             | 2516           | 0.089   |
| BAI-1    | 2-meth | 550 (sh)\(^a\), | 588             | 621, 669 (sh)\(^b\), | 904     | 0.389   |
|          | Film   | 404, 775        | 997             | 2873           | 0.015 ±  | 0.0909  |
|          | Film   | 392, 821        | 1074            | 2869           | 0.016 ±  | 0.23    |
|          | Film   | 447, 716        | 982             | 3783           | 0.013 ±  | 0.27    |
| PBAIC2   | 2-meth | 457, 753        | 1060            | 3846           | 0.011 ±  | 0.001   |
| PBAIBD1  | 2-meth | 378, 688        | 944             | 3942           | 0.018 ±  | 0.002   |
|          | Film   | 429, 749        | 1118            | 4407           | 0.0056 ± | 0.0001  |

\(^{a}\) \( \Phi_F \) as a 0.05 in methycyclohexane in ref. \(^{23}\) \(^{b}\) sh = shoulder in the spectra; see text for more details.

### Table 2. Experimental electrochemical parameters and energy levels\(^*\) of BAI copolymers determined in solution.

| Polymer   | \( E_{\text{onset}}^\text{ox} \) (V) | \( E_{\text{HOMO}} \) (eV) | \( E_{\text{LUMO}} \) (eV) | \( E_g \) (eV) | \( E_{\text{gap}} \) (eV) | \( E_{\text{gap}} \) (eV) |
|-----------|---------------------------------|-----------------|-----------------|----------------|----------------|----------------|
| PBAIC-1   | 0.0929                          | -4.96           | -3.57           | 1.39           | 1.48           | 0.27           | -1.15          |
| PBAIC-2   | 0.0909                          | -4.95           | -3.54           | 1.42           | 1.29           | 0.23           | -1.18          |
| PBAIBD-1  | 0.514                           | -5.38           | -3.85           | 1.52           | 1.54           | 0.25           | -1.12          |

\(^{*}\) \( E_{\text{onset}} \) = 0.064 V determined in 0.1M NBu₄PF₆ in CHCl₃ \(^{a}\) Estimated from the onset of absorption. See eq. 3, 4 and Table S1 for further details.

### Time-resolved spectroscopy studies

Femtosecond transient absorption (fs-TA) was further used to characterize the excited state dynamics of the copolymers and two model monomers (BAI1 and BDT) in solution and in thin films (Figures S1B-S1I and Table S6). From Figure 3, it is seen that the fs-TA spectra of the copolymers are composed of a broad positive excited state absorption (ESA) in the 880-1600 nm range, and negative TA bands between 350 nm and 955 nm matching with those in Figures 1 attributed to ground-state absorption (GSA).

In solution after about ~5 ps (PBAIC2) and ~10 ps (PBAIBD1) the initially formed ESA band blue-shifts by ~20 nm and thereon the band maxima remain unchanged. Since there are no additional bands at longer decay times (that could be attributed, e.g., to triplet excited state formation in the polymers) the positive TA bands are attributed to the S₁ → Sₐ ESA. This behavior contrasts with that of the monomeric BAI1 chromophore where in addition to the S₁ → Sₐ ESA (in the 350-480 nm and 665-800 nm), GSA, and stimulated emission in the (510-630 nm) bands, a triplet-triplet absorption band is also observed with triplet lifetime of \( \tau_{\text{T}} \approx 54 \mu\text{s} \) (presented in the ns-TA absorption spectra, Figure S10). For PBAIBD1 a characteristic ESA band is seen in the 460-560 range, as also found for the monomeric BDT unit. However, contrary to monomeric BDT, in PBAIBD1 this band...
disappears after 106 ps (see Figure SI10-SI11 and Figure 2). For monomeric BDT the $S_1\rightarrow S_0$ ESA band was found to be strongly overlapped with the $T_1\rightarrow T_0$ ESA band, as shown by comparison with the triplet absorption spectra obtained by ns-TA, ($\tau_T = 99$ μs), Figure SI10. The data support (i) the pronounced conjugation between BAI1 and BDT moieties in the PBAIBD1 copolymer, which promotes electron-delocalization, as shown by the significant red-shift of the absorption band when compared with the monomeric BAI1 (Figure 1), and (ii) the absence of triplet state formation in the polymers, due to the fast deactivation of the excited state. The mechanism behind this will be discussed below.

Global analysis of representative kinetic traces of the copolymers shows that transient decays are well fitted with the sum of three exponentials. The best-fit results and pre-exponential values are presented in Table 3 (also in table SI6 and Figure SI11 in SI). Either in solution, or in thin films, the copolymers show a first decay transient with values in the 0.71-8.9 ps range, a second one with values in the 14.9-58.4 ps range and a longer decay transient with values ranging from 55.6 ps to 1948 ps. BAI1 transient lifetimes of 66 ps, 5201 ps and 54 μs were determined. The latter was fixed in the analysis to the triplet lifetime obtained by ns-TA (Figure S19). The two shortest decay times are in agreement with the double-exponential decay behavior obtained from the fluorescence decays of BAI1 (fluorescence lifetimes, $\tau_F = 140$ ps and 4680 ps, Figure S12). BDT transient decays are well fitted with a double exponential decay law, with transient lifetimes of 313 ps (also in agreement with $\tau_T = 560$ ps obtained by TCSPC, Figure SI13) and 99 μs, that was fixed in the analysis to the triplet lifetime obtained by ns-TA (Figure SI14 in SI).

The shortest decay time component ($\tau_1$) which, at shorter emission wavelengths is associated to a negative pre-exponential for the PBAIC-1 copolymer (Table 3), should be considered to be associated to solvent dynamics (in THF with characteristic times ranging from 0.43 ps to 0.94 ps), or attributed to vibrational relaxation due to the depopulation of a hot vibrational state generated through the 770 nm excitation (since excitation was not performed in the lowest energy 0–0 electronic transition).38 Yet, this is not the case with PBAIC-2 and PBAIBD-1, where a longer component is observed with 2.4 ps and 8.9 ps (Table 3), respectively, in addition to a longer $\tau_3$ component in the order of hundreds of ps. These $\tau_1$ and $\tau_2$ decay components are associated to excitation energy migration within different segments of the polymer chain (higher to lower energy conjugated segments) ending up in the $\tau_3$ decay component which mirrors the decay of the more relaxed segment to the ground state.

From the donor-acceptor (D-A) character of the copolymers, one can determine the energy transfer ($k_{ET}$) rate constant from:38, 46-48

$$k_{ET} = \frac{1}{\tau_D} - \frac{1}{\tau_0}$$

where $\tau_0$ stands for the donor lifetime in the absence of acceptor and $\tau_D$ for the decay time of the donor in the polymer (with acceptor units). Due to the chemical structure of the corresponding repeat units (Scheme 1), the monomeric CPDT or BDT are taken as model donor units of the copolymers. Therefore for PBAIC-1,2 $\tau_D = 166$ ps (related to CPDT) and for PBAIBD-1 $\tau_D = 560$ ps (related to BDT, Figure S11) were used in eq. 4. The two decay components ($\tau_1$ and $\tau_2$) describe contributions of the energy donors in the presence of energy acceptors.49 This three exponential fit of the transient decays basically mirrors the fact that energy transfer (ET) processes leads to nonexponential decays and that the two shortest decay times, and respective pre-exponential factors, characterize, as a whole, the ET process. Indeed, from the pre-exponential factors in solution (Table 3), except for the longer

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Table 3. Pre-exponential values ($a_i$) resulting from the global analysis to the representative kinetics of the time-resolved transient absorption data, together with the rate constants for energy transfer processes ($k_{ET}$) for the investigated BAI copolymers in 2MeTHF solution.

| Polymer | $\lambda$ (nm) | $a_1$ | $k_{ET}(1)$ (s$^{-1}$) | $k_{ET}(2)$ (s$^{-1}$) |
|---------|---------------|------|----------------|----------------|
| PBAIC-1 | $\tau_1$ (ps) | 0.71 | 19.4| 114.7 |
| 911     | -0.494       | 0.059 | NA* | 4.55$\times10^{10}$ |
| 1200    | 0.194        | 0.645 | 0.160 |
| PBAIC-2 | $\tau_1$ (ps) | 2.4 | 36.7| 230.8 |
| 911     | -0.560       | 0.895 | 0.105 | 4.11$\times10^{11}$ |
| 1200    | 0.232        | 0.746 | 0.022 |
| PBAIBD-1 | $\tau_1$ (ps) | 8.9 | 49.7| 163.1 |
| 505     | 0.506       | 0.196 | 0.298 |
| 911     | 0.440       | -0.271 | 0.560 | 1.11$\times10^{11}$ |
| 1200    | 0.292       | 0.848 | 0.642 |

*NA-not applicable. Shorter $\tau_1$ (< 10 ps) component attributed to solvation dynamics.

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component (associated to a relaxed exciton segment decaying to the ground state) and the shorter component of PAIBC1 (associate to solvent dynamics) the ET process can be fully characterized by the two mentioned components. Considering the simplest case of Coulombic (Förster) energy transfer, in which the energy donor units are distributed in a medium with a uniform concentration of acceptors, $C_A$, the fluorescence decay function of the donor, $I_0(t)$, in the presence of acceptors can be obtained by eq. 5.49,50

$$I_0(t) = \exp(-\frac{t}{\tau_0}) \exp[-(4/3)\pi^2 R_0^3 C_A (t/\tau_0)^{3/2}]$$  

(5)

with $R_0$ the Förster radius and $\tau_0$ the lifetime of the Donor in the absence of acceptor.

Although energy transfer leads to nonexponential decays, the $I_0(t)$ for PBAIC-2 and PBAIBD-1 can be fitted with a sum of two exponentials terms (Figure 4), which corresponded to two shortest decay times in these copolymers (Table 3).

For PBAIC2, $\tau_2$ is dominant particularly at longer wavelengths (representing ~91 % of the total decay) and should be therefore seen as the governing the ET process (i.e., the ET process involving more distant D-A pairs); for PBAIBD1 similar contributions were found for the two decay times, 50 %, indicating that short and distant D-A pairs contribute equally to the on-chain hopping decay mechanism. Additionally, the rate constants for ET process varies from 1.83 x 10¹⁰ to 4.11 x 10¹¹ s⁻¹ (Table 3), characteristic of conjugated organic polymers.38,49

Conclusions

In this work, three new BAI-based donor-acceptor copolymers were synthesized, and their photoexcitation decay mechanisms investigated in solution and thin films. Even though the $\Phi_0$ of these copolymers varies from 1 up to 2% in solution, the film values are basically identical to solution, thus showing that ACQ is not taking place. While in solution, the BAI-containing copolymers presented broad long wavelength absorption bands, with maxima varying between 688-775 nm, in thin films, the red-shifted emission bands reaches 900-1300 nm, indicating that these copolymers are a promising class of low-bandgap, circa 1.4-1.5 eV, copolymers with solid state absorption and emission widely shifted into the NIR region. The decays in the PBAIBD-1 and PBAIC-2 copolymers were further associated to an excitation energy transfer hopping that could be rationalized with a Förster-type mechanism with differing donor-acceptor contributions.

Our work reaches not only the need of the development of new NIR-absorber polymers to featured applications e.g. in sensing and photovaltaics, but also reinforces the use bay-annulated indigo as building block for the generation of push–pull type conjugated polymers

Conflicts of interest

There are no conflicts to declare.

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