Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Ultrafast excitation energy transfer in a benzimidazole–naphthopyran donor–acceptor dyad

Electronic supplementary information (ESI)

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S1 Syntheses

The syntheses of the PPBI–DPNP dyad by Steglich esterification and the monomeric, free constituent DPNP were reported in previous work.[1] The reference compound PPBI was synthesized according to a literature procedure.[2]

S1.1 PPBI−DPNP

A mixed solution of 1-(2-hydroxyethyl)-2-(2-pyridyl)benzimidazole (1.19 g, 5 mmol), 3,3-diphenyl-[3*H*]naphtho[2,1-b]pyran-8-carboxylic acid (1.89 g, 5 mmol) and 4-dimethyl-aminopyridine (DMAP, 0.07 g, 0.6 mmol) in a mixture of tetrahydrofuran (THF, 20 mL) and dichloromethane (DCM, CH_2Cl_2, 8.0 mL) was stirred in an ice-water bath for 1 h. N,N'-dicyclohexycarbodiimide (DCC, 1.23 g, 6.0 mmol) was added, and the reaction mixture was warmed up slowly to room temperature and stirred continuously for 36 h. The precipitate was filtered off and the solvent was evaporated. The residue was dissolved in CH_2Cl_2 and the solution was dried with anhydrous Mg_2SO_4. The white solid product was obtained by column chromatography on silica (1 : 2 EE/petroleum ether). 1.8 g, yield 90 %. ^{1}H NMR (500 MHz, DMSO$-d_6$): δ 8.71 − 8.69 (d, 1H, J = 5.5 Hz), 8.31 − 8.28 (d, 1H, J = 8 Hz), 8.06 − 8.03 (t, 2H), 7.91 − 7.88 (m, 1H), 7.85 − 7.83 (d, 1H, J = 8 Hz), 7.80 − 7.77 (d, 1H, J = 9 Hz), 7.75 − 7.72 (d, 1H, J = 8 Hz), 7.58 − 7.55 (m, 1H), 7.50 − 7.46 (m, 5H), 7.45 − 7.42 (m, 1H), 7.40 − 7.34 (m, 5H), 7.31 − 7.27 (m, 3H), 6.65 − 6.62 (d, 1H, J = 10 Hz), 5.57 − 5.55 (d, 1H, J = 8 Hz), 5.39 − 5.36 (t, 2H), 4.74 − 4.72 (t, 2H).

S1.2 1-propyl-2-(2′-pyridyl)benzimidazole (PPBI)

A mixed solution of 2-(2-pyridyl)benzimidazole (1.11 g, 5.69 mmol) and K_2CO_3 (1.17 g, 8.47 mmol) in N,N-dimethylformamide (DMF, 12 mL) was stirred for 30 min. 1-Bromopropane (0.62 mL, 6.79 mmol) was added dropwise and the resultant mixture was then stirred for 5 h at 295 K. After the solvent was removed by evaporation, water (30 mL) was added and the organic product was extracted with ethyl acetate (EE, 30 mL). The organic layer was dried over $MgSO_4$. The purified product was obtained as a pale yellow oil by column chromatography on silica (1 : 1 DCM/ EE). 430 mg, yield 32 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.69 (m, 1H), 8.43 (dt, 1H, J = 8 Hz), 7.85 (m, 2H), 7.45 (m, 1H), 7.33 (m, 3H), 4.8 (m, 2H), 1.91 (m, 2H), 0.93 (t, 3H, J = 7.4 Hz).

S1.3 1-(2-hydroxyethyl)-2-(2′-pyridyl)benzimidazole (HPBI)

A mixed solution of 2-(2-pyridyl)benzimidazole (4.48 g, 23 mmol) and sodium hydroxide (2 g, 50 mmol,) in DMF (50 mL) under nitrogen was stirred at 35 °C for 1 h. A solution of 2-bromoethyl alcohol (3.12 g, 25 mmol) in DMF (10 mL) was added dropwise, and then the reaction mixture was heated up to 120 °C for half an hour. The mixture was cooled to room temperature and poured carefully into ice-cold water (300 mL). The solution was neutralised to pH $6 - 7$ with HCl solution, the precipitate was collected by filtration and dissolved in $CHCl_3$ (200 mL). The filtrate was extracted with $CHCl_3$ (300 mL) and the combined $CHCl_3$ solutions were dried over Mg_2SO_4. The purified pale brown crystals were obtained by column chromatography on silica (2 : 1 EE/petroleum ether). 3.5 g, yield 69 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.56 (s, 1H), 7.96 (m, 2H), 7.52 (m 2H), 7.43 (m, 2H), 4.86 – 4.89 (m 2H), 4.24 (t, 2H).

S1.4 3,3-diphenyl-[3*H*]naphtho[2,1-b]pyran-8-carboxylic acid (DPNP)

A mixed solution of 6-hydroxynaphthalene-2-carboxylic acid (0.98 g, 5 mmol) and 1,1-diphenylprop-2-yn-1-ol (1.14 g, 5 mmol) in CH_2Cl_2 (70 mL) was stirred under nitrogen at 35 °C. A catalytic amount of *p*-toluenesulphonic acid (PTSA, 100 mg) was added and the reaction mixture was stirred for two days. The crude product was collected by filtering. The purified product was obtained by column chromatography on silica (8 : 2 DCM/ EE). White powder, 0.99 g, yield 50 %. ^{1}H NMR (500 MHz, DMSO$-d_6$): δ 8.49 (s, 1H), 8.18 (d, 1H, J = 8.5 Hz), 7.99 (d, 1H, J = 9 Hz), 7.96 – 7.94 (m, 1H), 7.52 – 7.48 (m, 5H), 7.40 (d, 1H, J = 8.5 Hz), 7.37 – 7.34 (m, 4H), 7.26 (m, 2H), 6.64 (d, 1H, J = 10 Hz).

S2 Ground- and excited-state structures of the PPBI–DPNP dyad molecule

S2.1 Crystallographic and calculated ground-state and excited-state minimum structures

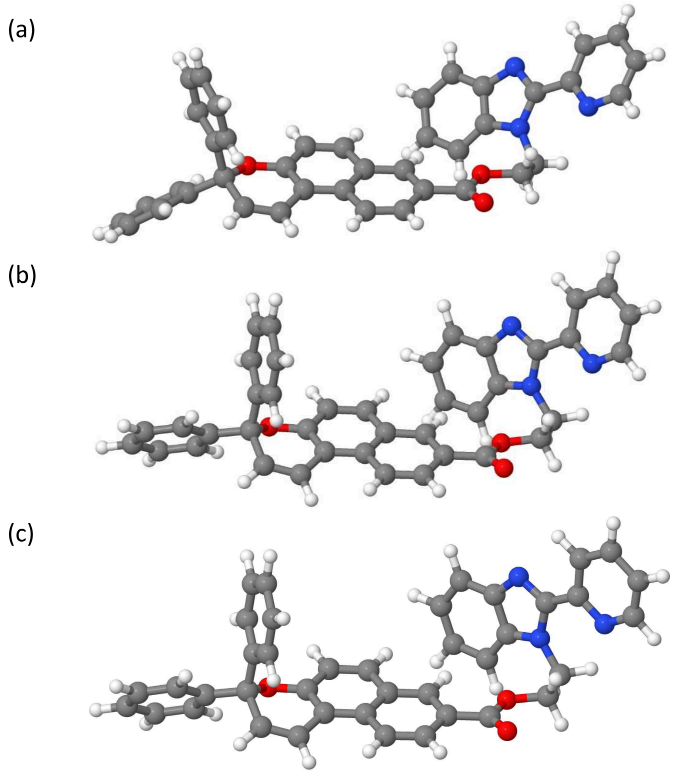

Fig. S1: (a) Crystallographic structure of the PPBI–DPNP dyad molecule from Ref. 1 (CCDC number: 870473). (b) Optimized molecular structure in the ground state at the MP2/def2-SVP level of theory. (c) Calculated minimum energy structure of the dyad molecule in the PPBI*–DPNP donor-excited state at the RI-SCS-ADC(2)/def2-SVP level of theory.

S2.2 Cartesian coordinates of the calculated ground- and excited-state structures

Table S1: Cartesian coordinates of the calculated RI-SCS-MP2/def2-SVP ground-state minimum structure of the dyad molecule.

atom	x / Å	y / Å	z / Å
C	7.1533346	7.4316864	6.1503460
C	8.0179067	6.3574474	5.8207896
C	9.2757282	6.2375979	6.4506778
H	9.9363790	5.4032251	6.2022824
C	9.6357537	7.2157188	7.3735813
H	10.6061604	7.1577038	7.8750409
C	8.7640747	8.2948491	7.6840675
H	9.0815508	9.0401936	8.4191931
C	7.5149307	8.4268412	7.0799571
H	6.8417817	9.2427962	7.3507574
C	6.2468118	6.0982408	4.6347702
C	5.3159731	5.5251352	3.6428527
C	5.7935341	4.5153018	2.7811600
H	6.8335779	4.1975485	2.8642880
C	4.9097844	3.9524864	1.8613286
H	5.2467469	3.1653637	1.1812265
C	3.5869766	4.4167369	1.8188284
H	2.8615299	4.0053650	1.1129946
C	3.2102726	5.4248691	2.7111984
H	2.1850746	5.8113805	2.7108529
C	4.8496475	8.1106902	5.4457627
H	4.3969359	8.2051791	4.4528709
H	5.1943252	9.1027008	5.7732198
C	3.8182520	7.5665099	6.4180522
H	2.9798745	8.2735357	6.5299410
H	3.4186596	6.6089502	6.0566438
C	3.7467302	6.8265579	8.6568504
C	4.5755819	6.4934706	9.8524687
C	5.9609741	6.4623992	9.7941911
H	6.4796328	6.7086578	8.8659328
C	6.7261197	6.1083418	10.9395189
C	6.0590817	5.7810917	12.1646750
C	4.6315507	5.8077731	12.1854832
H	4.0991564	5.5327105	13.0990129
C	3.9060837	6.1487421	11.0602432
H	2.8136546	6.1539180	11.0764556

C	6.8418006	5.4353136	13.3167259
C	8.2315951	5.3682165	13.1947043
C	8.8929837	5.7075002	11.9864653
H	9.9845063	5.6584041	11.9607985
C	8.1537094	6.0684561	10.8791548
H	8.6473698	6.3217856	9.9366435
C	8.4297013	4.1108376	15.1926291
C	7.0607746	4.6233217	15.5949059
H	6.7247227	4.4869975	16.6265798
C	6.2964286	5.2309863	14.6592967
H	5.3087095	5.6235521	14.9149280
C	8.3880287	2.7410607	14.5096661
C	9.5781038	2.2691023	13.9226501
H	10.4777087	2.8889940	13.9700271
C	9.6081296	1.0250908	13.2871346
H	10.5362470	0.6691880	12.8305192
C	8.4503061	0.2315842	13.2360762
H	8.4733996	-0.7425149	12.7395174
C	7.2672523	0.6943386	13.8216967
H	6.3606777	0.0835808	13.7820833
C	7.2334293	1.9482903	14.4531015
H	6.3016263	2.3085547	14.8954737
C	9.3461846	4.0789885	16.4098165
C	9.2616991	3.0013427	17.3097867
H	8.5889454	2.1661245	17.0948068
C	10.0492854	2.9822902	18.4670139
H	9.9789543	2.1362698	19.1567399
C	10.9300640	4.0392408	18.7371156
H	11.5502335	4.0218699	19.6376686
C	11.0146567	5.1139928	17.8430475
H	11.7000464	5.9419059	18.0467053
C	10.2203342	5.1418778	16.6880035
H	10.2815811	5.9816149	15.9942975
N	7.4281036	5.5476236	4.8795872
N	6.0286236	7.2563467	5.3667368
N	4.0465103	5.9700559	3.6081532
O	4.4857183	7.3811297	7.6683260
O	2.5554158	6.6305025	8.5615051
O	9.0187899	5.0475667	14.2623963

Table S2: Cartesian coordinates of the calculated RI-SCS-ADC(2)/def2-SVP excited-state minimum energy structure of the dyad molecule.

atom	x / Å	y / Å	z / Å
C	4.9685464	8.1891381	5.6149527
H	5.1322202	9.1146941	5.0475089
H	4.8871444	8.4184557	6.6914206
C	3.7015967	7.5099511	5.1190214
H	2.8163733	8.1408491	5.3226306
H	3.7610763	7.3299800	4.0328633
C	2.5606959	5.4737674	5.4893700
C	2.6262102	4.1436340	6.1646607
C	3.7451980	3.7359618	6.8760204
H	4.6102402	4.4009585	6.9736635
C	3.7875159	2.4533966	7.4892637
C	2.6646882	1.5711028	7.3672865
C	1.5330850	2.0177378	6.6188721
H	0.6723232	1.3532096	6.4842200
C	1.5128040	3.2674366	6.0275827
H	0.6474846	3.6006064	5.4432173
C	2.7150305	0.2832180	7.9989587
C	3.8857633	-0.1021980	8.6571816
C	4.9920676	0.7756697	8.7911728
H	5.8729759	0.4229385	9.3402890
C	4.9441481	2.0287118	8.2142148
H	5.7970325	2.7156762	8.2965832
C	3.2558893	-2.3869568	8.6225756
C	1.8231890	-1.9387847	8.4115994
H	1.0124334	-2.6682923	8.5329416
C	1.5885053	-0.6485197	8.0772475
H	0.5627410	-0.2872236	7.9350949
C	3.9890363	-2.7204368	7.3204898
C	5.3700634	-2.9881574	7.4024907
H	5.8662946	-2.9513508	8.3802854
C	6.1004005	-3.2969964	6.2512284
H	7.1763043	-3.5010703	6.3251220
C	5.4585568	-3.3500499	5.0020145
H	6.0309286	-3.5936247	4.0980455
C	4.0862372	-3.0891840	4.9169022
H	3.5792997	-3.1242777	3.9441232
C	3.3526640	-2.7692951	6.0720582
H	2.2813650	-2.5530183	5.9915857

C	3.2871569	-3.5706977	9.5822038
C	3.0213323	-4.8633550	9.0941414
H	2.8614008	-5.0202835	8.0199062
C	2.9795211	-5.9557196	9.9700911
H	2.7766515	-6.9601857	9.5771649
C	3.2047429	-5.7685149	11.3420199
H	3.1785675	-6.6248785	12.0275762
C	3.4682036	-4.4815077	11.8299543
H	3.6457984	-4.3268345	12.9020014
C	3.5010555	-3.3833914	10.9576287
H	3.7009793	-2.3780088	11.3409534
O	3.6041216	6.2677847	5.8264320
O	1.6861707	5.8203166	4.7273201
O	3.9825778	-1.3164204	9.2710790
N	6.1257367	7.3160890	5.4455643
C	6.5918805	6.4925485	6.4019301
C	6.8539604	6.9993617	4.2083250
C	7.6404863	5.6963038	5.7510625
C	6.2591308	6.3435499	7.7744138
N	7.7590529	6.0293595	4.4438634
C	6.6537532	7.6410737	2.9583171
C	8.3398935	4.7324881	6.4999494
C	6.9790654	5.3771425	8.4936634
H	5.4568261	6.9213298	8.2434880
N	5.6996473	8.6259324	2.8405724
C	7.4576409	7.2271229	1.8417291
C	7.9999127	4.5958622	7.8676527
H	9.1196923	4.1232264	6.0311139
H	6.7627117	5.2182819	9.5571678
C	5.5437877	9.1889012	1.6378058
C	7.2664347	7.8381569	0.6126222
H	8.2008371	6.4364151	1.9905605
H	8.5385901	3.8571196	8.4752598
H	4.7733715	9.9734883	1.5769179
C	6.2829533	8.8509903	0.4930850
H	7.8697848	7.5384020	-0.2543751
H	6.0985416	9.3630933	-0.4590205

S3 Fluorescence data

S3.1 Static fluorescence spectra and spectral overlap integral

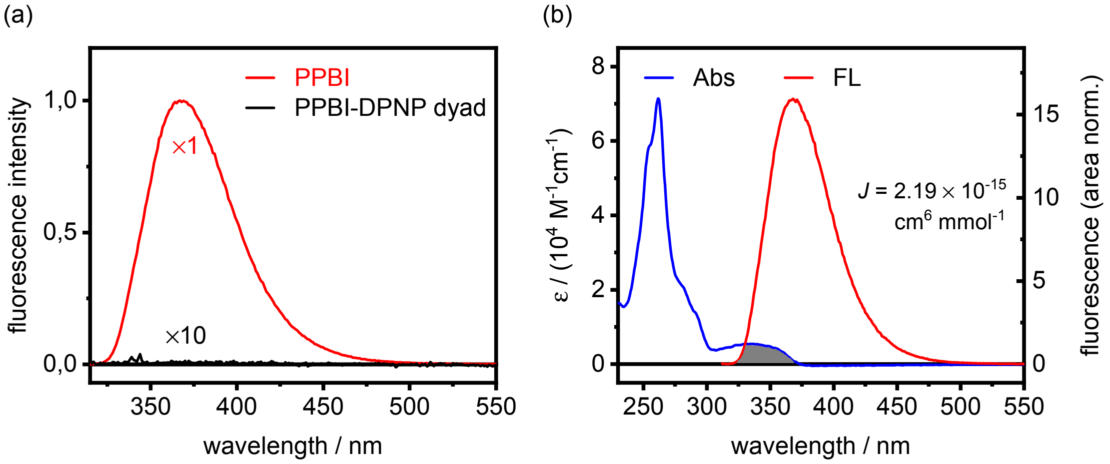

Fig. S2: (a) Static fluorescence spectra of PPBI (red), DPNP (blue) and the PPBI–DPNP dyad (black) measured under the same experimental conditions (apparatus settings and sample concentrations) in ACN upon excitation at λ_{exc} = 310 nm. The fluorescence intensities for DPNP and the dyad are shown with 100-fold magnifications. (b) Determination of the spectral overlap integral $J = 2.19 \times 10^{-15}$ cm^6 mmol^{-1} between the area-normalized fluorescence of PPBI (red) and the molar extinction coefficient of DPNP (blue).

S3.2 Fluorescence quantum yields

The fluorescence quantum yields (Φ_{FL}) of free PPBI and the PPBI-DPNP dyad molecule were measured relative to 2-aminopyridine ($\Phi_{\text{FL}} = 0.66$) resp. phenanthrene ($\Phi_{\text{FL}} = 0.125$) as fluorescence standards. The characteristic parameters of the reference compounds are listed in Table S3. The standards were chosen because they absorb and emit in similar spectral regions as the samples. All pairs of measurements were made using the same instrument settings (slit widths, integration time, excitation wavelength, etc.).

Table S3: Properties of the employed fluorescence standards 2-aminopyridine and phenanthrene.

	emission	excitation	solvent	λ_{exc}	value	references
2-aminopyridine	315 – 480	285	H_2SO_4 (0.1 M)	280 – 315	0.66 ± 0.05	Ref. 3
phenanthrene	345 – 410	260 – 335	EtOH	254, 313	0.125 ± 0.007	Ref. 4

From the measurements, the fluorescence quantum yields are given by

$$\Phi_{\mathrm{FL}} = \frac{I_{\mathrm{FL}}\, f_{\mathrm{ref}}\, n^2}{I_{\mathrm{FL,ref}}\, f\, n_{\mathrm{ref}}^2}\, \Phi_{\mathrm{FL,ref}}\,, \tag{S I}$$

where the subscript "ref" denotes the fluorescence standard, $f = 1 - 10^{-A}$ is the absorption factor (with A = absorbance), I_{FL} is the spectrally integrated fluorescence intensity, and n denotes the refractive index of the respective solution. The obtained results are listed in Table S4.

Table S4: Results of the fluorescence quantum yield measurements.

	A(λ_{exc})	I_{FL} / (10^5)	n	Φ_{FL}
2-aminopyridine	0.0348	81.0	1.334	0.660
PPBI	0.0405	50.7	1.344	0.360
phenanthrene	0.0181	37.2	1.362	0.125
PPBI–DPNP dyad	0.0450	3.5	1.344	0.005

S3.3 Fluorescence lifetime of PPBI

The fluorescence lifetime τ_{D} of the free donor compound PPBI was measured by time-correlated single photon counting (TCSPC) using a PicoQuant FluoTime 200 instrument. The excitation pulses at λ_{exc} = 290 nm and 10 MHz repetition rate were delivered by a PLS 290-10 laser diode. The measured pulse duration was 840 ps (full width at half maximum, fwhm). The recorded fluorescence–time profiles (see Fig. S3 for an example) were modeled by a sum of two exponentials (cf. Table S5) convoluted with the instrument response function (IRF). The measurements gave an amplitude-weighted lifetime of

$$\langle \tau_{\mathrm{D}} \rangle = 1.38 \pm 0.02 \text{ ns.}$$

Table S5: Fit parameters describing the measured fluorescence decay time profiles of PPBI.

parameter	value
α_1 / counts	146500
τ_1 / ns	1.37
α_2 / counts	368
τ_2 / ns	4.16
$\langle \tau_{\mathrm{D}} \rangle$ / ns	1.38

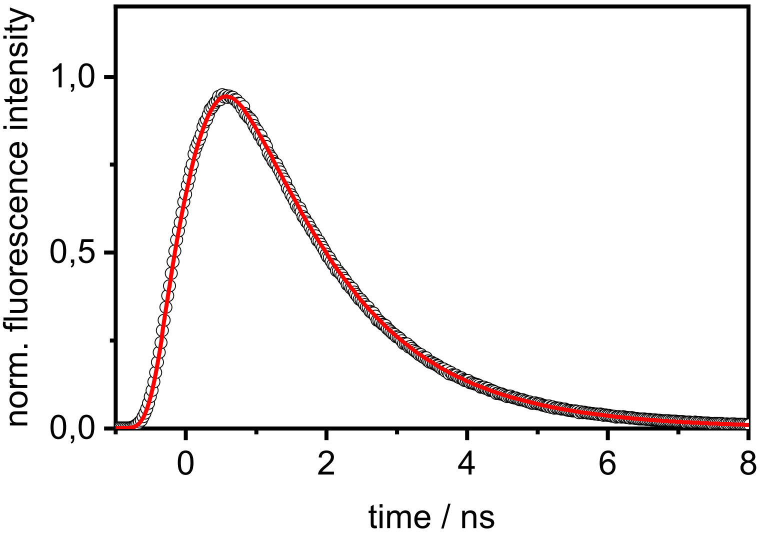

Fig. S3: TCSPC fluorescence–time profile of PPBI in ACN.

S4 Femtosecond transient absorption results

S4.1 Unscaled experimental spectro-temporal transient absorption maps

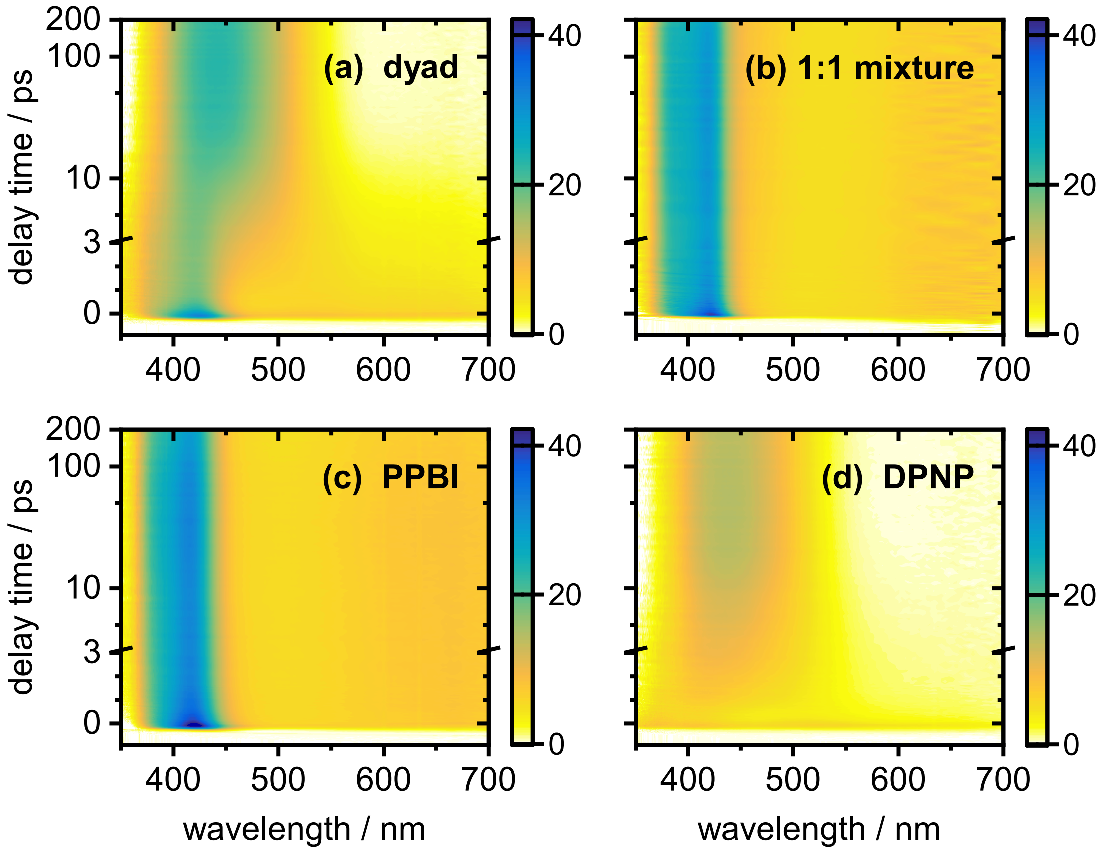

Fig. S4: Two-dimensional spectro-temporal transient absorption maps showing the change in optical density ΔOD for (a) the PPBI–DPNP dyad, (c) an equimolar mixture of PPBI and DPNP, (c) PPBI and (d) DPNP in ACN after photoexcitation at $\lambda_{\mathrm{pump}} = 310$ nm for probe wavelengths between 350 and 700 nm and pump–probe delay times from –1 to 200 ps. The sample concentration are: 0.12 mM (OD = 0.31) for the dyad, 0.16 mM (OD = 0.38) for PPBI, 0.30 mM (OD = 0.11) for DPNP, and 0.15 mM each (OD = 0.39) for the 1:1 mixture.

S4.2 Acceptor-excited contribution to the dyad transient absorption map

Since all transient absorption data were taken with the same experimental setup under otherwise identical experimental conditions, the signal contribution of the acceptor-excited PPBI–DPNP* dyad molecules can be subtracted from the transient absorption map of the photo-excited dyad to obtain the pure PPBI*–DPNP donor-excited dyad contribution. This is done by using the molar absorption coefficients of the individual PPBI and DPNP dyad constituents at the excitation wavelength (cf. UV absorption spectra in Fig. 2 of the main paper) and assuming independent absorptions. Applying the Lambert-Beer law at the excitation wavelength, the intensity absorbed by the DPNP subunit in solution of the dyad is given by

$$I_{\mathrm{PPBI-DPNP^*}} = I_0 \times \epsilon_{\mathrm{DPNP}} \times c \times d \times \left(\frac{1 - 10^{-A}}{A} \right),$$

where $A = (\epsilon_{\mathrm{DPNP}} + \epsilon_{\mathrm{PPBI}}) \times c \times d$ is the total absorption, c the concentration of the solution, and d the sample thickness. Likewise, for the pure DPNP solution, the absorbed intensity is given by

$$I_{\mathrm{DPNP^*}} = I_0 \times \epsilon_{\mathrm{DPNP}} \times c \times d.$$

Since the transient absorption signals are direct proportional to the concentrations of the photoexcited units, and thus to the absorbed intensities, one obtains

$$\Delta OD^*_{\mathrm{PPBI-DPNP}} = \frac{I_{\mathrm{PPBI-DPNP^*}}}{I_{\mathrm{DPNP^*}}} \times \Delta OD^*_{\mathrm{DPNP}} = 0.326 \times \Delta OD^*_{\mathrm{DPNP}}$$

for the signal contribution of the acceptor-excited PPBI–DPNP* dyad molecules. Thus, the spectro-temporal transient absorption map for the PPBI–DPNP dyad corresponding solely to the PPBI*–DPNP excited state, given in Fig. 3(e) of the main paper, is obtained from the experimentally recorded map by subtraction of the transient absorption map of the DPNP acceptor scaled by the above factor of 0.326.

S4.3 SVD analysis of the transient absoption matrices for the dyad and its constituents PPBI and DPNP

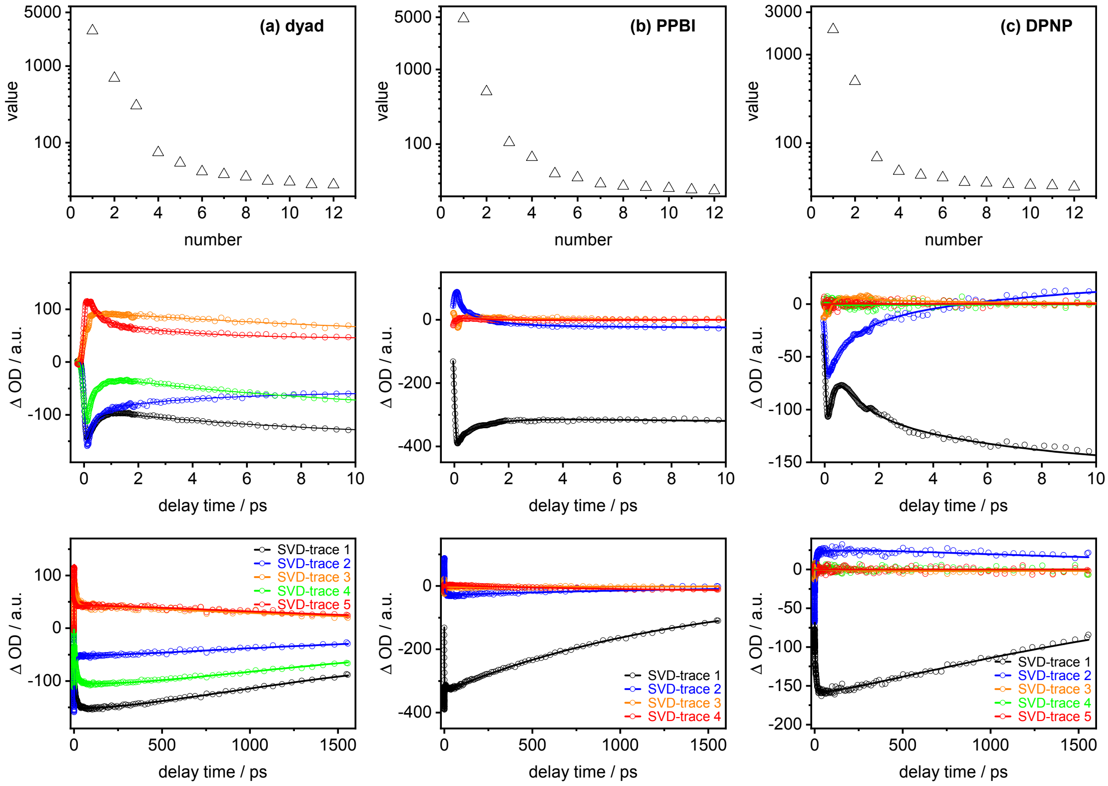

Fig. S5: Top row: Singular-value scree plots for (a) PPBI–DPNP, (b) PPBI and (c) DPNP resulting from the SVD analysis on a logarithmic scale. Middle and bottom rows: SVD time traces for the dyad and its constituents PPBI and DPNP described by simultaneous non-linear least-squares fitting using a sum of exponentials convoluted with the IRF.

S4.4 Time traces for the dyad and its constituents PPBI and DPNP

Figure S6 shows a set of experimental and fitted time traces for the dyad and its constituents PPBI and DPNP following excitation at $\lambda_{\mathrm{pump}} = 310$ nm after integration over the distinct ESA bands in the spectro-temporal absorption maps of Fig. 3. Simultaneous non-linear least-squares fits to the main ESA bands gave exactly the same time constants as the global SVD analysis. The data for PPBI indicate a delayed rise with a time constant of $\tau_3 = 12.4$ ps (orange, Fig. S6(b)) appearing at about $\Delta t \sim 30$ ps, which can be assigned to a minor (2% in amplitude) excited-state hydrogen bonding interaction of PPBI with residual water in the ACN.

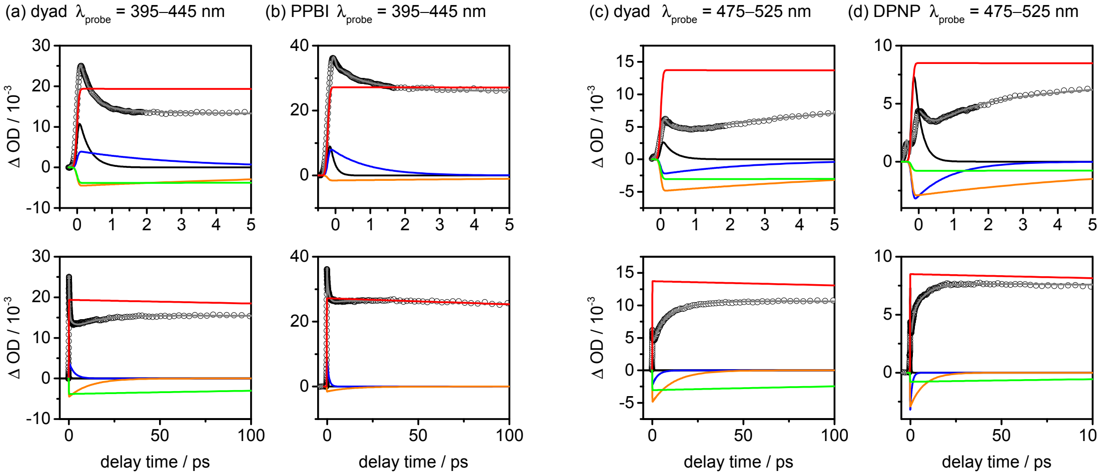

Fig. S6: Transient absorption time traces of PPBI–DPNP, PPBI and DPNP after excitation at $\lambda_{\mathrm{pump}} = 310$ nm in the probe windows from 395 – 445 nm for (a) the dyad and (b) PPBI and from 475 – 525 nm for (c) the dyad and (d) DPNP.

References

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