



Cite this: *Chem. Commun.*, 2020, 56, 5560

Received 13th January 2020,
Accepted 6th April 2020

DOI: 10.1039/d0cc00335b

rsc.li/chemcomm

Efficacious elimination of intramolecular charge transfer in perylene imide based light-harvesting antenna molecules†

Rajeev K. Dubey,[‡] Damla Inan, Abbey M. Philip, Ferdinand C. Grozema[‡] and Wolter F. Jager[‡]

Two light-harvesting antenna molecules were obtained by positioning naphthalene monoimide energy donors at the imide position, instead of the bay positions, of perylene imide energy acceptors. Such rational design resulted in a complete suppression of parasitic intramolecular charge transfer without compromising the desired ultrafast rates of excitation energy transfer.

Artificial photosynthesis, in view of the abundance and intermittency of solar energy on the one hand and the long-time storage capacity of fuels on the other hand, is the most promising concept for providing sustainable energy to coming generations.^{1–4} By mimicking natural photosynthesis using synthetic components, this process will produce fuels from abundant feedstock, generally water, carbon dioxide and solar energy.³ In the molecular approach, light harvesting antenna molecules composed of chromophores that exhibit complementary light absorption, are essential components.^{5–7}

Ideal light-harvesting antenna molecules absorb a substantial part of the solar spectrum, transfer excited energy from donor to acceptor chromophores quantitatively, and have an acceptor group that has a stable and long-lived excited state, from which charges can be extracted efficiently.⁸ With the development of a series of modular antenna molecules composed of naphthalene monoimide (NMI) donors and exceptionally stable perylene-3,4,9,10-tetracarboxylic acid (PTCA) acceptors, which absorb complementary parts of the solar spectrum up to 600 nm, we have demonstrated to meet the above-mentioned requirements.⁹

However, in polar solvents, intramolecular charge transfer has been observed for those antenna molecules in which electron-rich energy-donors were connected through the bay-positions of PTCA based energy-acceptors (Fig. 1).¹⁰ In a similar

bay-functionalized antenna system studied by Würthner *et al.*, undesired intramolecular charge transfer was noticed even in non-polar toluene (Fig. 1).¹¹ For the light-harvesting antenna systems, this intramolecular charge transfer is a parasitic process, which seriously reduces the light-harvesting efficiency, and must be eliminated. Herein, we will demonstrate that by simply changing the topology of the molecules, while employing identical donor and acceptor constituents, this undesired intramolecular charge transfer can be fully suppressed.

To achieve this goal, we have designed and synthesized antenna molecules **Im-D2A2** and **Im-D2A4**, which are composed of the NMI donor **D2** and the PTCA acceptors **A2** and **A4**, respectively. Unlike the previously prepared antenna molecules composed of similar constituents, like **D2A2** and **D2A3**, the NMI donors in **Im-D2A2** and **Im-D2A4** are attached to the PTCA imide-positions (Fig. 1).^{9,10} This rational design of **Im-D2A2** and **Im-D2A4** is inspired by recent reports, which clearly exhibited that the charge transfer from imide substituents on PTCAs is slower than from bay- or ortho-substituents.^{12–14} It must be noted that such positional effects have never been tested for excitation energy transfer processes. Therefore, positional effects on the various parameters (*e.g.* rate and efficiency) related to the energy transfer are unknown. This is the first study that demonstrates the type and magnitude of such effects in the perylene based light-harvesting antenna systems.

The syntheses of antenna molecules **Im-D2A2** and **Im-D2A4** started with the imidization of the appropriate bay-halogenated PTCA anhydrides, followed by substitution of the bay halogens (Schemes S1 and S2, ESI†). From the readily available perylene monoanhydride diester **1**, using the amino-functionalised NMI donor **2**, the monoimide diester **3** was synthesised in 55% yield using standard imidization conditions.¹⁵ Subsequently, the bromine atoms at the bay positions were substituted by 4-*tert*-butylphenol moieties to obtain the first antenna system **Im-D2A2** in a 61% yield.^{14,16}

The synthesis of the perylene bisimide (PBI) based antenna compound, **Im-D2A4**, started with the imidization of tetrachloro-*p*-erylene bisanhydride **4**, followed by bay-substitution in a 26% overall yield (Scheme S2, ESI†).^{17,18} It should be mentioned that

Department of Chemical Engineering, Delft University of Technology,
Van der Maasweg 9, 2629 HZ Delft, The Netherlands.
E-mail: rajeev.dubey@polymat.eu, W.F.Jager@tudelft.nl

† Electronic supplementary information (ESI) available: Synthesis and characterization of new compounds, and photophysical data. See DOI: 10.1039/d0cc00335b

‡ Present address: POLYMAT, Basque Center for Macromolecular Design and Engineering, University of the Basque Country UPV/EHU, Avenida de Tolosa 72, 20018 Donostia-San Sebastian, Spain.



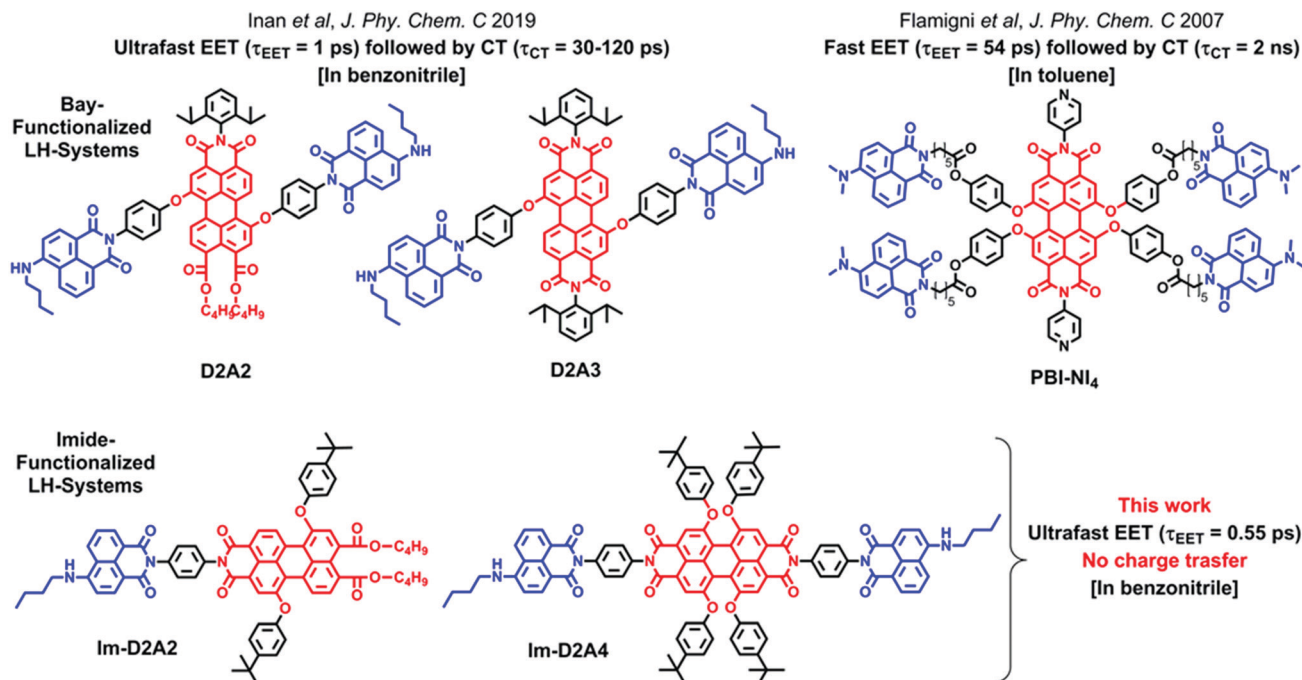


Fig. 1 Two imide-functionalized antenna systems **Im-D2A2**, **Im-D2A4** and previously studied bay-functionalized antenna systems **D2A2**, **D2A3**, and **PBI-NI₄**.

we initially had designed **Im-D2A3**, the imide analogue of compound **D2A3**, but that compound could not be synthesized due to the low solubility of the intermediates, regardless of the order of peri and bay substitutions at the perylene scaffold (Scheme S4, ESI†).

The photophysical properties of the antenna molecules (**Im-D2A2** and **Im-D2A4**) and the reference compounds (**D2**, **A2** and **A4**; Fig. S1, ESI†) have been examined in polar benzonitrile. In this solvent, fast charge transfer, with τ_{CS} values of 120 and 30 ps, has been observed for the bay-functionalized antenna molecules **D2A2** and **D2A3**, respectively.¹⁰ Steady-state spectroscopy reveals that the UV-vis absorption spectra of the antenna compounds equal the sum of the spectra of their constituents (Fig. 2 and Fig. S2, ESI†). This indicates a decoupled chromophoric character and the absence of ground state interactions, which is also clear from the electronic structure calculations (Section 5, ESI†).

Upon excitation of the donor chromophore in **Im-D2A2** and **Im-D2A4**, fluorescence of the donor moiety was not observed.

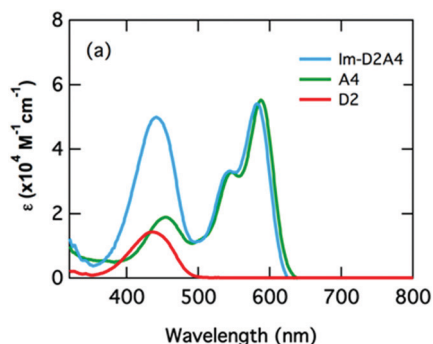


Fig. 2 UV-Vis absorption spectra of antenna systems **Im-D2A4** along with reference acceptor **A4** and reference donor **D2** in benzonitrile.

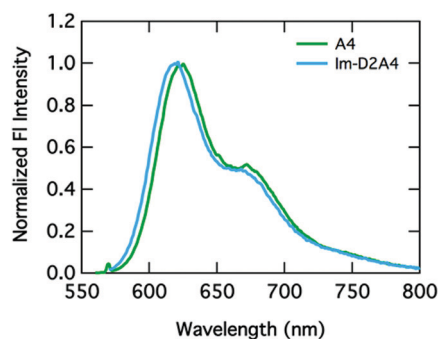


Fig. 3 Normalized steady-state emission spectra of **Im-D2A4** and **A4**.

Instead, acceptor's fluorescence was observed exclusively (Fig. 3). This observation indicates that excitation energy transfer from the donor to the acceptor is quantitative for **Im-D2A2** and **Im-D2A4**; *i.e.* all excitation energy is transferred from **D2** to the acceptor chromophore to result in singlet excited-state of the acceptor. This observation is further verified by the comparison of the absorption and fluorescence excitation spectra of antenna molecules, which were found almost identical for both antenna molecules (Fig. S9, ESI†).

However, unexpectedly in **Im-D2A2** and **Im-D2A4**, the resultant singlet excited-state of the acceptor decays to the ground-state with a 15–35% decrease in fluorescence quantum yields compared to those of the model acceptors **A2** and **A4** (Table 1). Similarly, time-resolved emission of the acceptor moieties in these antenna molecules showed bi-exponential decay, whereas the emission of model-acceptor molecules (**A2** and **A4**) was mono exponential, with time constants τ_F of 4.6 and 5.7 ns, respectively. For the antenna molecules, the slow decay components were prevalent and had lower time constants than the model acceptors.

Table 1 Photo-physical properties of the antenna systems and reference compounds in benzonitrile

Comp.	λ_{abs} (nm)	ϵ (M ⁻¹ cm ⁻¹)	λ_{em} (nm)	ϕ_F^a	τ_F^b (ns)	τ_{EET}^c (ps)
D2	437	15 200	514	0.87	8.29	—
A2	522	37 800	568	0.82	4.55	—
Im-D2A2	520	37 900	564	0.70	1.5 (10%), 4.2 (90%)	0.51
A4	588	55 300	618	0.93	5.7	—
Im-D2A4	583	54 200	617	0.61	1.8 (22%), 4.5 (78%)	0.61

^a Fluorescence quantum yield. ^b Fluorescence lifetime (λ_{exc} = 400 nm).

^c Lifetime data for energy-transfer obtained from femtosecond transient absorption.

In all, the results obtained so far reveal that the excited energy-donor quantitatively transfers its energy to the acceptor to result in perylene's singlet excited-state. Subsequently, the excited-perylene decays to the ground-state with a decreased fluorescence quantum yield and bi-exponential lifetimes.

To gain the insight of the excited-state dynamics of these systems, femtosecond transient absorption spectroscopy was carried out (Fig. 4 and Fig. S11, ESI†). After the laser excitation of the donor moiety at 430 nm, the excited-state of the donor, along with the singlet excited-state of the simultaneously excited acceptor, are observed. In the picosecond time domain, the singlet excited-state of the acceptor is formed exclusively, due to an ultrafast excitation energy transfer (EET) process. At longer delay times, the spectra of excited acceptor start decaying in the time-frame of the acceptor's emission. No further changes in the spectra were observed, apart from changes in the shape of

the excited state acceptor absorption around 530 nm. These changes are identical to those seen in the decay of the model acceptor **A2**.¹⁰ Results from the relevant experiments on the individual model compounds (**D2**, **A2** and **A4**) are provided in the ESI† (Fig. S12).

The kinetics of the energy transfer that occurs by the Förster resonance energy transfer (FRET) mechanism has been determined using single wavelength fitting.¹⁹ The excitation energy transfer (EET) for **Im-D2A2** and **Im-D2A4**, with time constants τ_{EET} of 0.51 and 0.61 ps, respectively (Table 1), is notably faster than for the previously studied antenna molecules **D2A2** and **D2A3** where the donor moieties were attached at the bay-positions. This increased energy transfer rate is due to the favorable head to tail alignment of the donor and acceptor transition dipoles, which strongly increases the orientation factor κ^2 in eqn (S2) (ESI†). The effect of the increased orientation factor clearly overcompensates the effect of the ~30% increased donor acceptor distance r_{DA} ,²⁰ that would otherwise lead to a slower EET process. The decay kinetics of the excited acceptors is in the nanosecond time scale and is in line with the singlet-state lifetimes of the model acceptors **A2** and **A4**.

The combined results, obtained by steady-state and time-resolved spectroscopy, clearly show that donor-acceptor systems **Im-D2A2** and **Im-D2A4** undergo ultrafast excitation energy transfer from the naphthalene-based donor to the perylene-based acceptor. In both compounds, the acceptor's singlet excited-state decays to the ground state *via* emission with a fluorescence quantum yield that is 15–30% lower than that of the acceptor model compounds **A2** and **A4**. Clearly, this implies that the antenna performance of **Im-D2A2** and **Im-D2A4** is superior compared to that of the corresponding bay-functionalized antenna molecules **D2A2** and **D2A3**, for which a fast charge separation process was observed, with τ_{CS} = 20–120 ps, and acceptor's fluorescence was fully quenched. A summary of the photophysical behavior of **Im-D2A4**, along with the experimental evidence provided, is illustrated in Fig. S13 (ESI†).

As far as intramolecular charge transfer is concerned, no direct or indirect evidence has been obtained for its involvement as the mechanism for the decrease of fluorescence in these imide-functionalized systems. In transient absorption studies, no spectral evidence for the formation of the perylene radical anions, which can be easily recognized by their characteristic strong and relatively narrow absorption at *ca.* 725 nm,^{21–23} has been detected. This observation as such does not fully exclude the occurrence of photo-induced electron transfer within the antenna molecules. Therefore, we tried to look for indirect evidence to fully exclude the involvement of charge transfer in these systems and have calculated the energies of charge-separation (ΔG_{CS}^0).²⁴ For antenna **Im-D2A2**, in benzonitrile, the ΔG_{CS}^0 is obtained as −0.45 eV (Table S2, ESI†). Whereas, for **Im-D2A4**, ΔG_{CS}^0 is −0.31 eV, which is significantly higher than in **Im-D2A2**. However, for both systems, a similar extent of fluorescence quenching was observed. Similarly, **D2A2** and **Im-D2A2** have nearly the same ΔG_{CS}^0 in benzonitrile (−0.46 & −0.45 eV, respectively). But for **D2A2**, acceptor's fluorescence was fully quenched. Clearly, a correlation between the decrease in fluorescence quantum yields

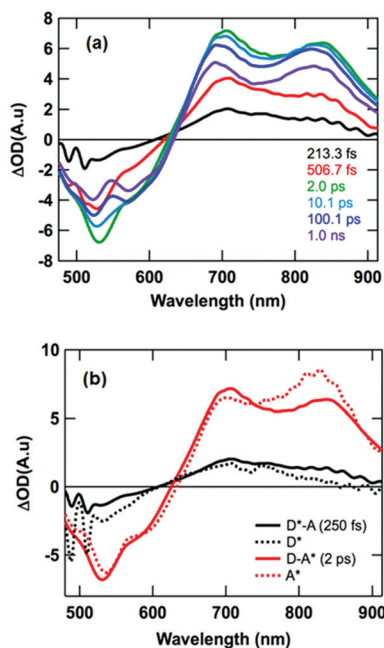


Fig. 4 (a) Time evolution of the femtosecond transient absorption spectra of **Im-D2A2** after excitation at 430 nm in benzonitrile. (b) The spectra of **Im-D2A2** with the dissociation of species after different time delays along with reference donor and reference acceptor.



of the antenna molecules (Table 1) and the charge transfer energies does not exist, and this further indicates that charge transfer is not likely the cause of this fluorescence quenching. Furthermore, additional fluorescence measurements on **Im-D2A2** and **Im-D2A4** in the less polar solvents, toluene and chloroform, in which intramolecular charge transfer processes are endergonic or slightly exergonic (Table S2, ESI†), reveal that the fluorescence quantum yields of these antenna compounds are also 10–35% lower than those of the corresponding model acceptors **A2** and **A4** (see Table S1, ESI†). Also, lifetime measurements in these solvents revealed dual fluorescence for the antenna molecules, while the model acceptor molecules had single exponent decay. These results indicated that additional fluorescence quenching is observed in solvents of different polarities even those in which charge transfer is thermodynamically not allowed. All these observations, collectively, exclude intramolecular charge transfer as the quenching mechanism in these imide-functionalized antenna systems **Im-D2A2** and **Im-D2A4**. Instead, it appears that attachment of the large energy-donors at the imide-positions results in the formation of at least two stable conformations of the acceptor's singlet excited state.²⁵ One of these conformations has a lower 1.5 ns lifetime, presumably due to a faster relaxation, which eventually results in a modest decrease of the fluorescence quantum yield.

In conclusion, we have presented a simple, but very effective, strategy to prevent the undesired intramolecular charge transfer in perylene imide-based light-harvesting antenna systems. This involves the attachment of naphthalene monoimide based energy-donor at the imide-position of the perylene-acceptor instead of bay-positions. A detailed photophysical analysis, by both steady state and time resolved measurements, has proven that intramolecular charge transfer does not take place in these antenna systems, not even in the highly polar solvent benzonitrile. Importantly, ultrafast excitation energy transfer occurred within 0.5–0.6 ps, which is notably faster as compared to the antenna systems with bay-attached donor moieties. This shows that positioning the energy-donor at the imide-position of perylene dyes does not compromise the rate and efficiency of energy transfer. However, attachment of the large energy-donors at the imide-positions does induce an additional slow (nanosecond range) quenching process for the perylene's singlet excited-state, which needs further investigation. The absence of charge transfer, combined with the opportunity to attach up to four additional substituents at the bay positions,²⁶ from which charge transfer reactions are highly efficient, show that antenna molecules **Im-D2A2** and **Im-D2A4** are ideal light harvesting antenna components for application in artificial photosynthesis. Our current research will focus on the integration of these antenna molecules in devices for artificial photosynthesis.

This work has received funding from the European Research Council Horizon 2020 ERC Grant Agreement no. 648433.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 D. K. Dogutan and D. G. Nocera, *Acc. Chem. Res.*, 2019, **52**, 3143–3148.
- 2 D. G. Nocera, *Acc. Chem. Res.*, 2017, **50**, 616–619.
- 3 D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 2009, **42**, 1890–1898.
- 4 N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15729–15735.
- 5 A. Harriman, *Chem. Commun.*, 2015, **51**, 11745–11756.
- 6 J. Iehl, J.-F. Nierengarten, A. Harriman, T. Bura and R. Ziessel, *J. Am. Chem. Soc.*, 2012, **134**, 988–998.
- 7 R. Croce and H. van Amerongen, *Nat. Chem. Biol.*, 2014, **10**, 492–501.
- 8 P. D. Frischmann, K. Mahata and F. Würthner, *Chem. Soc. Rev.*, 2013, **42**, 1847–1870.
- 9 R. K. Dubey, D. Inan, S. Sengupta, E. J. R. Sudholter, F. C. Grozema and W. F. Jager, *Chem. Sci.*, 2016, **7**, 3517–3532.
- 10 D. Inan, R. K. Dubey, W. F. Jager and F. C. Grozema, *J. Phys. Chem. C*, 2019, **123**, 36–47.
- 11 L. Flamigni, B. Ventura, C.-C. You, C. Hippius and F. Würthner, *J. Phys. Chem. C*, 2007, **111**, 622–630.
- 12 L. E. Shoer, S. W. Eaton, E. A. Margulies and M. R. Wasielewski, *J. Phys. Chem. B*, 2015, **119**, 7635–7643.
- 13 B. Pagoaga, O. Mongin, M. Caselli, D. Vanossi, F. Momicchioli, M. Blanchard-Desce, G. Lemercier, N. Hoffmann and G. Ponterini, *Phys. Chem. Chem. Phys.*, 2016, **18**, 4924–4941.
- 14 D. Inan, R. K. Dubey, N. Westerveld, J. Bleeker, W. F. Jager and F. C. Grozema, *J. Phys. Chem. A*, 2017, **121**, 4633–4644.
- 15 S. Sengupta, R. K. Dubey, R. W. M. Hoek, S. P. P. van Eeden, D. D. Gunbaş, F. C. Grozema, E. J. R. Sudhölter and W. F. Jager, *J. Organic Chem.*, 2014, **79**, 6655–6662.
- 16 R. K. Dubey, A. Efimov and H. Lemmetyinen, *Chem. Mater.*, 2011, **23**, 778–788.
- 17 R. K. Dubey, N. Westerveld, F. C. Grozema, E. J. R. Sudhölter and W. F. Jager, *Org. Lett.*, 2015, **17**, 1882–1885.
- 18 R. K. Dubey, N. Westerveld, E. J. R. Sudholter, F. C. Grozema and W. F. Jager, *Org. Chem. Front.*, 2016, **3**, 1481–1492.
- 19 This method can be used since ultrafast excitation energy transfer is the only process that occurs after donor excitation, apart from slow acceptor emission.
- 20 For the inter-chromophoric distance, center to center we have calculated $r_{DA} = 14.3 \text{ \AA}$ for **Im-D2A2**, and $r_{DA} = 11.6 \text{ \AA}$ for **D2A2**.
- 21 W. E. Ford, H. Hiratsuka and P. V. Kamat, *J. Phys. Chem.*, 1989, **93**, 6692–6696.
- 22 R. K. Dubey, M. Niemi, K. Kaunisto, K. Stranius, A. Efimov, N. V. Tkachenko and H. Lemmetyinen, *Inorg. Chem.*, 2013, **52**, 9761–9773.
- 23 N. Zink-Lorre, E. Font-Sanchis, S. Seetharaman, P. A. Karr, Á. Sastre-Santos, F. D'Souza and F. Fernández-Lázaro, *Chem. – Eur. J.*, 2019, **25**, 10123–10132.
- 24 R. H. Goldsmith, L. E. Sinks, R. F. Kelley, L. J. Betzen, W. Liu, E. A. Weiss, M. A. Ratner and M. R. Wasielewski, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 3540–3545.
- 25 R. A. L. Vallée, M. Cotlet, M. Van Der Auweraer, J. Hofkens, K. Müllen and F. C. De Schryver, *J. Am. Chem. Soc.*, 2004, **126**, 2296–2297.
- 26 R. K. Dubey, S. J. Eustace, J. S. van Mullem, E. J. R. Sudhölter, F. C. Grozema and W. F. Jager, *J. Organic Chem.*, 2019, **84**, 9532–9547.

