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

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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 demonstrate to meet the above-mentioned requirements.⁹

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.⁵ 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 PTCA 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-tort-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-perylene bisanhydride 4, followed by bay-substitution in a 26% overall yield (Scheme S2, ESI†).¹⁷,¹⁸ It should be mentioned that
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 $\tau_{CS}$ values of 120 and 30 ps, has been observed for the bay-functionalized antenna molecules **D2A2** and **D2A3**, respectively. 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. 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 $\tau_F$ 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. | 12 abs (nm) | 12 cm (M\(^{-1}\) cm\(^{-1}\)) | 12 em (nm) | \(\phi_f\) | \(\tau_b\) (ns) | \(\tau_{EET}\) (ps) |
|-------|-------------|-----------------|-----------|-------|----------|-------------|
| D2    | 437         | 15 200          | 514       | 0.87  | 8.29     | —           |
| A2    | 522         | 37 800          | 568       | 0.82  | 4.55     | —           |
| Im-D2A2 | 520       | 37 900          | 568       | 0.70  | 1.5 (10%)| 4.2 (90%)  |
| A4    | 588         | 55 300          | 618       | 0.93  | 5.7      | —           |
| Im-D2A4 | 583       | 54 200          | 617       | 0.61  | 1.8 (22%)| 0.61 4.5 (78%) |

*Fluorescence quantum yield. \(^b\) Fluorescence lifetime (\(\tau_{em} = 400\) 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-perylen 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 \(\tau_{EET}\) 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 \(\chi^2\) in eqn (S2) (ESI†). The effect of the increased orientation factor clearly overcompensates the effect of the ~30% increased donor acceptor distance \(\tau_{D-A}\) 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 \(\tau_{CS} = 20–120\) 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 \(\alpha\) 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 (\(\Delta G_{CS}\).\(^{24}\)

For antenna Im-D2A2, in benzonitrile, the \(\Delta G_{CS}\) is obtained as −0.45 eV (Table S2, ESI†). Whereas, for Im-D2A4, \(\Delta G_{CS}\) 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 \(\Delta G_{CS}\) 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 exponential 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 trans-
fer 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 conforma-
tions 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 com-
ponents for application in artificial photosynthesis. Our current
research will focus on the integration of these antenna mole-
cules in devices for artificial photosynthesis.

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Conflicts of interest
There are no conflicts to declare.

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