Multiplicity conversion based on intramolecular triplet-to-singlet energy transfer

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The ability to convert between molecular spin states is of utmost importance in materials chemistry. Förster-type energy transfer is based on dipole-dipole interactions and can therefore theoretically be used to convert between molecular spin states. Here, a molecular dyad that is capable of transferring energy from an excited triplet state to an excited singlet state is presented. The rate of conversion between these states was shown to be 36 times faster than the rate of emission from the isolated triplet state. This dyad provides the first solid proof that Förster-type triplet-to-singlet energy transfer is possible, revealing a method to increase the rate of light extraction from excited triplet states.

RESULTS AND DISCUSSION

Molecular design

Molecules in their excited states can interact with each other in a variety of different ways. Förster-type energy transfer is unique because the interacting molecules can be located fairly far apart (up to 50 to 100 Å). Other types of interactions such as Dexter-type energy transfer or electron transfer need more or less direct orbital overlap to occur. To examine energy transfer through a dipole-dipole
mechanism, we synthesized a DBA molecule (Fig. 1A; see section S1 for synthesis and characterization details). Design criteria used for DBA were the following: (i) The donor emission should overlap with the acceptor absorption to allow energy transfer through a dipole-dipole mechanism to occur. (ii) The bridging unit should contain no π-electrons or lone electron pairs to minimize electron tunneling between the donor and acceptor. (iii) The bridging unit should be rigid to avoid direct contact between the donor and acceptor. Furthermore, considering possible applications, energy transfer should occur with minimal spectral energy loss. The acceptor should therefore be a highly fluorescent molecule with a reasonably small Stokes shift to minimize spectral energy loss in the triplet-to-singlet conversion. Because the most important spectral feature of the dyad components is a considerable overlap between the donor emission and acceptor absorption, both functional components were selected with great care. An Ir III complex (D) was chosen as the donor (24) and perylene (A), which has a fluorescence quantum yield close to unity and small Stokes shift (25), was selected as the acceptor. The bridging unit was of pivotal importance to spatially separate the donor and acceptor moieties. We chose bicyclo[2.2.2]octane as the bridging unit because its rigid structure permits free rotation only along the long axis of the molecule, meaning it can behave as a stable linker for the functional components of the dyad.

Assessing the preserved integrity of the components in the dyad

When evaluating the efficiency of energy transfer, the emission of the dyad was compared to the emission of the individual components. For this comparison to be accurate, it is important that the integrity of the donor and acceptor chromophores in the dyad is preserved. If the properties of A and D are not conserved in DBA, then the system should not be considered as one molecule containing two chromophores but rather as one chromophore, and the Jabłoński diagram in Fig. 1B would not be valid. Figure 2 shows the absorption spectra of A, D, and DBA. Donor D exhibits a relatively weak transition around 320 nm, and A displays the characteristic vibronic pattern of perylene-containing molecules. Figure 2 also depicts the arithmetic sum of the D and A absorption spectra. A close-to-perfect overlap between the sum of D and A absorption spectra and the absorption spectrum of DBA was observed, indicating that the integrity of the components in the dyad was preserved. Thus, the ground- and excited-state energy levels of D and A are retained in the dyad, making it an excellent model system to study possible triplet-to-singlet energy transfer.

Triplet-to-singlet energy transfer

To assess whether the dyad can transfer energy, we determined emission quantum yields (Φ), as well as excited-state lifetimes (τ) (Fig. 3, A to C). Upon exciting D, the initially formed excited singlet state is rapidly converted to a triplet state (Fig. 1B) in high yield (24). The observed lifetime of 41.5 μs and the emission quantum yield of 62% are therefore solely related to the process of phosphorescence. The rate of phosphorescence calculated from τ and Φ was $1.49 \times 10^4$ s$^{-1}$. A exhibited a much shorter lifetime (3.1 ns), as expected for the quantum-mechanically allowed process of fluorescence, and an emission quantum yield of 85%. The excited-state lifetime of both D and A could be explained with a single exponential fit. However, this was not the case for the dyad, which required two exponentials $\tau_{DBA,1}$ (lifetime of the short-lived component) = 3.7 ns; $\tau_{DBA,2}$ (lifetime of the long-lived component) = 290 ns to explain the observed emission decay. $\tau_{DBA,1}$ is similar to the lifetime of A and can therefore be explained by direct excitation of the acceptor moiety in DBA (see section S2). $\tau_{DBA,2}$ is two orders of magnitude larger than $\tau_{DBA,1}$ but still much shorter than the lifetime of D. The shortened lifetime in DBA when exciting the donor moiety does not prove that an energy transfer event has occurred. Instead, the decrease of the lifetime could be caused by other decay pathways of the excited triplet state of the donor moiety opening up in the dyad. To prove that the emission at long time scales occurs because of triplet-to-singlet energy transfer, TRES was performed. In a TRES experiment, emission decay is measured for each emission wavelength, covering the whole emission profile (Fig. 3D). This offers the possibility to compare the spectral envelope of the decay at short and long times after
excitation. Figure 3E shows normalized emission spectra of D and A, as well as snapshots of dyad emission 0 to 7 and 15 to 1500 ns after excitation. The two snapshots represent the emission profiles of the short- and long-lived components of the emission decay of DBA, and both resemble the emission profile of A. Thus, at both short and long time scales, emission occurs from the excited singlet state of acceptor moiety in DBA, proving that triplet-to-singlet energy transfer has occurred. The long-lived component in the emission decay represents the rate of energy transfer, which, together with the emission quantum yield of DBA, was used to calculate the rate constant of energy transfer to \(5.33 \times 10^5\) s\(^{-1}\) (see section S2 for details). The rate of energy transfer in DBA is thus 36 times faster than the rate of phosphorescence. Furthermore, the rate of energy transfer depends on the intrinsic rate of emission of D and the energy overlap between D and A. Triplet-to-singlet energy transfer thus constitutes a general method to enhance the rate of emission of any phosphorescent material.

We have so far shown that an energy transfer event from the excited triplet state of the donor moiety to the excited singlet state of the acceptor moiety can occur in DBA. To prove that the most plausible mechanism for this energy transfer is a Förster-type dipole-dipole mechanism, we compared the experimentally obtained rate constant (\(k_T = 5.33 \times 10^5\) s\(^{-1}\)) with a theoretically derived value. The main parameters for Förster-type energy transfer are the overlap between donor emission (Fig. 3E) and acceptor absorption (Fig. 2) and the distance and relative angle of the responsible transition dipole moments. The bridging unit is stiff but able to rotate in solution. Assuming free rotation of the carbon–carbon single bond in the bridging unit, the average rate constant of energy transfer in DBA was calculated to be \(3.35 \times 10^5\) s\(^{-1}\) (see section S3 for details). This value agrees well with that measured experimentally, confirming the occurrence of fast triplet-to-singlet energy transfer.

The energy transfer process in DBA is a one-way process driven by the enthalpy decrease of the system. It is instructive to quantify how much energy is lost in the unidirectional energy transfer step, i.e., how much energy is expended in the triplet-to-singlet conversion. Figure 3F presents a CIE diagram of the emission colors of D and DBA (calculated from the data in Fig. 3E). The hue of the emission from DBA is in fact bluer than that of D despite the energy required for the triplet-to-singlet transfer to occur. The reason for the bluer emission of DBA than that of D is the narrower emission bandwidth of A compared to that of D. Förster-type resonance energy transfer can thus be used to increase the rate of emission without an apparent loss of photon energy. This is because strong fluorophores generally have a small Stokes shift and narrower emission profile compared to those of phosphorescent metal–organic compounds.

**CONCLUSION**

To conclude, the first example of intramolecular triplet-to-singlet energy transfer was presented here. The energy transfer was 36 times faster than the rate of donor phosphorescence. The results were fully explained using the theory of Förster-type resonance energy transfer. Furthermore, the transfer could be achieved without an apparent loss of photon energy. These results demonstrate that triplet-to-singlet transfer is possible and can be used to increase the rate of emission from phosphorescent compounds. Our results are thus of direct practical importance in the field of organic electronics, where the slow emission of light from triplet states is problematic.

**MATERIALS AND METHODS**

**General**

All starting materials were purchased from Sigma-Aldrich Chemical Co. and used without further purification unless otherwise noticed. All moisture- and oxygen-sensitive reactions were carried out using Schlenk techniques in oven-dried glassware. Solvents used for moisture- and oxygen-sensitive reactions were dried using an MBraun MB
SUPPLEMENTARY MATERIALS

Accurate Mass Q-TOF LC/MS.

Fig. S4. Transient absorption decays of DBA when excited at 320 nm.

Fig. S2. Transient absorption spectroscopy and decay of D in toluene when excited at 320 nm.

Fig. S1. Emission quantum yield of A, measured using an integrated sphere.

Table S1. Excited-state lifetimes (fractional contributions in parentheses) and associated J-coupling values are given in Fig. S4.

Fig. S22. 31P NMR (162 MHz, CDCl3),

Fig. S21. 13C NMR (201 MHz, CDCl3),

Fig. S18. 1H NMR (800 MHz, DMSO-d6),

Fig. S14. 13C NMR (201 MHz, CDCl3),

Fig. S12. 13C NMR (201 MHz, CDCl3),

Fig. S20. 1H NMR (800 MHz, CDCl3),

Fig. S15. 13C NMR (201 MHz, CDCl3),

Fig. S16. 1H NMR (800 MHz, CDCl3),

Fig. S9. 1H NMR (400 MHz, CDCl3),

Fig. S6. Lifetime of DBA with different excitation intensity.

Fig. S5. The simulated rate of energy transfer as a function of dihedral angle (orange line).

Section S4. X-ray diffraction of and DBA

Section S2. Details of the experimental determination of the rate of energy transfer

Scheme S1. Synthesis of the DBA.

Table S1. Excited-state lifetimes (fractional contributions in parentheses) and associated emission quantum yields for D, A, and DBA in toluene solutions.

Fig. S1. Emission quantum yield of A, measured using an integrated sphere.

Fig. S2. Transient absorption spectroscopy and decay of D in toluene when excited at 320 nm.

Fig. S3. Transient absorption spectroscopy of DBA in toluene solution when excited at 320 nm.

Fig. S4. Transient absorption decays of DBA when excited at 320 nm.

REFERENCES AND NOTES

1. F. So, Organic Electronics: Materials, Processing, Devices and Applications (CRC Press, 2009).

2. S. Ogawa, Organic Electronics Materials and Devices (Springer, 2015).

3. P. Klán, J. Weiz, Photochemistry of Organic Compounds: From Concepts to Practice (Wiley, 2009).

4. M. R. Roest, A. M. Oliver, M. N. Padden-Row, J. W. Verhoeven, Distance dependence of singlet and triplet charge recombination pathways in a series of rigid bichromophoric systems. J. Phys. Chem. A 101, 4687–4671 (1997).

5. M. A. Baldo, D. F. O’Brien, You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, Highly efficient phosphorescent emission from organic electro luminescent devices. Nature 395, 151–154 (1998).

6. D. J. Gaspar, E. Polikarpov, OLED Fundamentals: Materials, Devices, and Processing of Organic Light-Emitting Diodes (CRC Press, 2015).

7. S. Schmidbauer, A. Hohenleutner, B. Köng, Chemical degradation in organic light-emitting devices: Mechanisms and implications for the design of new materials. Adv. Mater. 25, 2114–2129 (2013).

8. H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, Highly efficient organic light-emitting diodes from delayed fluorescence. Nature 492, 234–238 (2012).

9. K. Satrianis, M. Hertzog, K. Börjesson, Selective manipulation of electronically excited states through strong light matter interactions. Nat. Commun. 9, 2273 (2018).

10. H. Nakamotani, T. Higuchi, T. Fukurokawa, K. Masui, K. Morimoto, M. Numata, H. Tanaka, Y. Sagara, T. Yasuda, C. Adachi, High-efficiency organic light-emitting diodes with fluorescent emitters. Nat. Commun. 5, 4016 (2014).

11. Z. Yang, Z. Mao, Z. Xie, Y. Zhang, S. Liu, J. Zhao, J. Xu, Z. Chi, M. P. Aldred. Recent advances in organic thermally activated delayed fluorescence materials. Chem. Soc. Rev. 46, 915–1016 (2017).

12. F. Töpper, Zwischenmolekularne Energiewanderung und Fluoreszenz. Ann. Phys. 437, 55–75 (1948).

13. R. G. Bennett, R. P. Schwenker, R. E. Kellogg, Radiationless intramolecular energy transfer. II. Triplet—singlet transfer. J. Chem. Phys. 41, 3040–3041 (1964).

14. D. Guo, T. E. Knight, J. K. McCusker, Angular momentum conservation in dipolar energy transfer. Science 334, 1684–1687 (2011).

15. N. J. Tuero, V. Ramamurthy, J. C. Scaiano, Principles of Molecular Photophysics: An Introduction (Univ. Science Books, 2009).

16. M. Skagisigirs, X. Guo, O. S. Wenger, Electron accumulation on napthalene diimide photosensitized by [Ru(2,2′-Bipyridine) 3]2+. Inorg. Chem. 56, 2432–2439 (2017).

17. Y.-L. Chang, Y. Song, Z. Wang, M. G. Helander, J. Qiu, L. Chai, Z. Liu, G. D. Scholes, Z. Lu, Highly efficient warm white organic light-emitting diodes by triplet exciton conversion. Adv. Funct. Mater. 23, 705–712 (2013).

18. Y.-L. Chang, S. Song, X. Wang, R. White, C. Yang, S. Wang, Z. H. Lu, Highly efficient greenish-blue platinum-based phosphorescent organic light-emitting diodes on a high triplet energy platform. Appl. Phys. Lett. 104, 173303 (2014).

19. Y.-L. Chang, Z.-H. Lu, White organic light-emitting diodes for solid-state lighting. J. Disp. Technol. 9, 459–468 (2013).
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