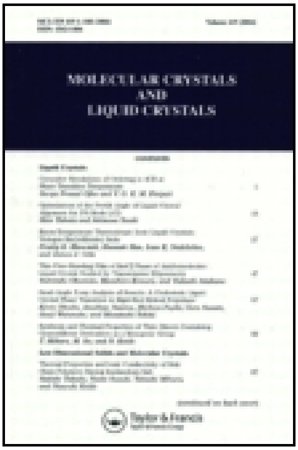

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Supermolecular Excitation Antenna: Ordered Energy Funnel

Michael R. Shortreed [a], Zhong-You Shi [a] & Raoul Kopelman [a]
[a] University of Michigan, Department of Chemistry, Ann Arbor, MI, 48109-1055

Version of record first published: 24 Sep 2006.

To cite this article: Michael R. Shortreed , Zhong-You Shi & Raoul Kopelman (1996): Supermolecular Excitation Antenna: Ordered Energy Funnel, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 283:1, 95-100

To link to this article: http://dx.doi.org/10.1080/10587259608037870

Mol. Cryst. Liq. Cryst., 1996, Vol. 283, pp. 95–100
Reprints available directly from the publisher
Photocopying permitted by license only

SUPERMOLECULAR EXCITATION ANTENNA: ORDERED ENERGY FUNNEL

MICHAEL R. SHORTREED, ZHONG-YOU SHI AND RAOUL KOPELMAN
University of Michigan, Department of Chemistry, Ann Arbor, MI 48109-1055

Abstract The development of exciton probes, including single molecule probes, inspired the design of a single molecule lens or energy antenna, based on phenylacetylene dendrimers, the largest so far synthesized structurally ordered molecules. To demonstrate the energy-funnel model we synthesized partial dendrimeric wedges with an excitation acceptor, a perylene derivative pendant, at the locus. As expected, the energy transfer from the large antenna (39 phenyl groups) increases the yield of the yellow perylenic emission by three orders of magnitude for a given excitation wavelength. Overall, such a photonic subwavelength antenna or nano-lens may play a role in developing molecular excitonics, including luminescent optical nanoprobes, scanning exciton tunneling microscopy and nanometer scale fiber-optic chemical and biochemical sensors.

INTRODUCTION

It has long been a challenge to mimic nature's photosystems with sophisticated molecularly engineered nanostructures[1-5]. An interesting application has been the subwavelength light source, based on exciton transporting molecular nanocrystals[6]. This photon nanosource was designed for near-field optics (NFO) applications, such as nanometer resolved microscopy[7], spectroscopy[8] and fiber-optic chemical sensors[9, 10]. In contrast to the classical far-field optics, which is diffraction limited, in NFO the light can be focused to the size of the light source[11, 12] and thus, in principle, to a molecular size. In practice, however, current NFO light sources are limited by the photon penetration depth (say 220 Å for metallic aluminum)[13, 14]. In contrast, the molecular excitonics approach[15], can "focus" the light within 5-10 Å. We note that quantum optics effects take over at such small sizes, i.e., there is a highly localized excitation, confined inside matter, which may result in energy transfer, electron transfer and other non-radiative processes, as well as light emission.

SPECTRA

The excitonic funnels in green plants[16-19] and in their polymeric mimics[1, 2] are both structurally and energetically disordered and thus the energy transport has to rely, in part, on random walk, thermal activation and/or exciton percolation[3, 17, 19, 20]. Ideally one disires a symmetric antenna with an ordered geometry and ordered energetics so as to form a perfect energy funnel. A new class of supermolecules, i.e., highly symmetric and perfectly hyperbranched macromolecules with well-controlled structures[21, 22] are good candidates for such nano-funnels. Figure 1 shows a specially designed phenyl-acetylene dendrimer derivative called nanostar ($C_{460}H_{424}$). To first approximation these dendrimer supermolecules are like "molecular crystals" with a basic unit of phenylacetylene or diphenylacetylene. For various dendrimers and

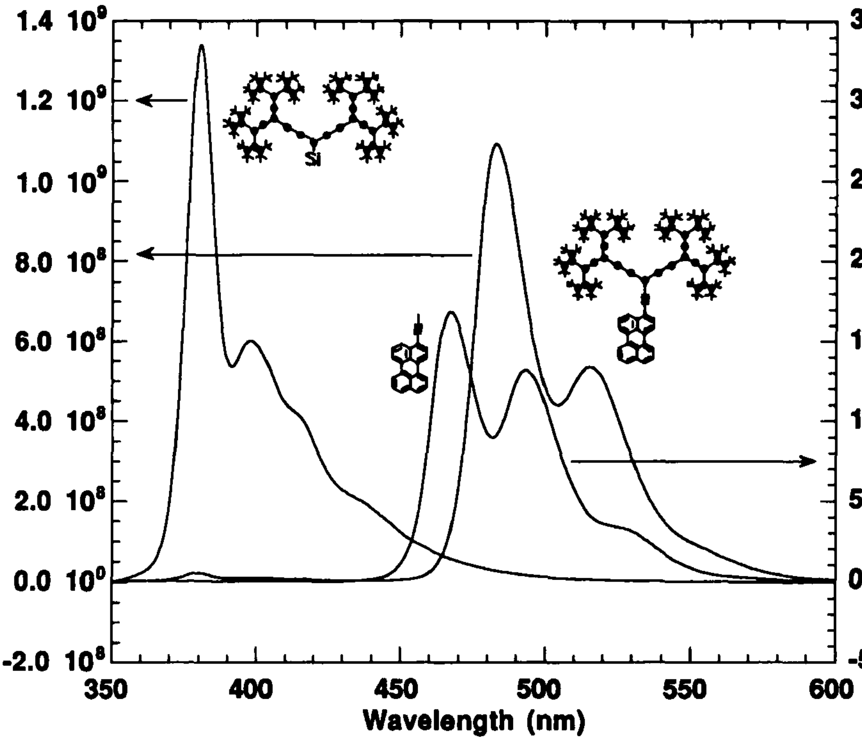

FIGURE 1 Normalized emission spectra of the monodendron (M39-Si), 1-ethynylperylene and the nanostar. Note the reduced scale, on the right, for the enthynylperylene. When the monodendron group is part of the nanostar (right), its fluorescence (at 370 nm) is totally quenched, and its energy funneled into the nanostar acceptor ethynylperylenic group, whose fluorescence is now three orders of magnitude more intense than the isolated ethynylperylene molecule (compare left-hand scale to right-hand scale).

especially for the monodendron and nanostar molecules (see fig. 1) the energy transport is very fast, even on the picosecond time scale of the antenna's excited state, and highly efficient.

ENERGY FUNNEL

We assign the strong absorption features (fig. 2) as localized periphery (canopy) excitations. These strong features are representative for the large majority of ring systems, i.e. all those with threefold coordination to other rings. The remainder of the ring systems have a coordination number of two and thus form small linear chains of rings. If we assume that the edge rings of such chains should also be included (partially), i.e. counting diphenyl-acetylene fragments or simply acetylenic bonds, we end up with linear chains of effectively two or three members. The fragments at the periphery have the higher energy level while the longer linear fragments towards the center have successively lower energies, thus suggestinging an ideal energy (exciton) funnel[20, 23, 24].

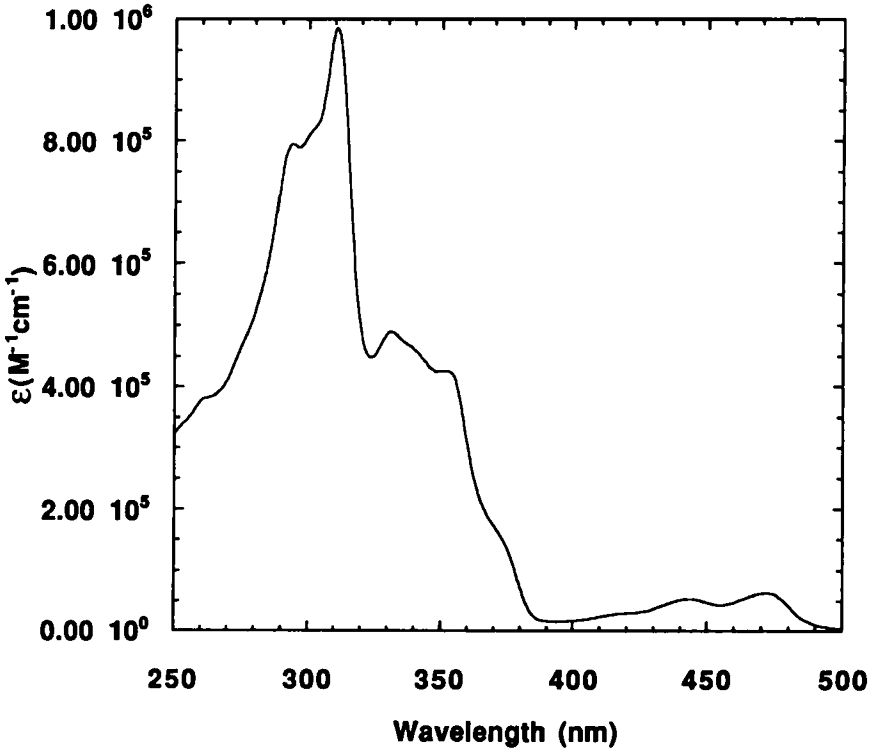

FIGURE 2 Nanostar absorption spectrum in dichloromethane.

The nanostar fluorescence spectrum (Fig 1.) provides the most important result, namely the observation that there is direct and efficient non-radiative intramolecular energy transfer in the nanostar from the dendrimer antenna system to the perylene acceptor. It is the basis for the energy funnel below (Fig. 3).

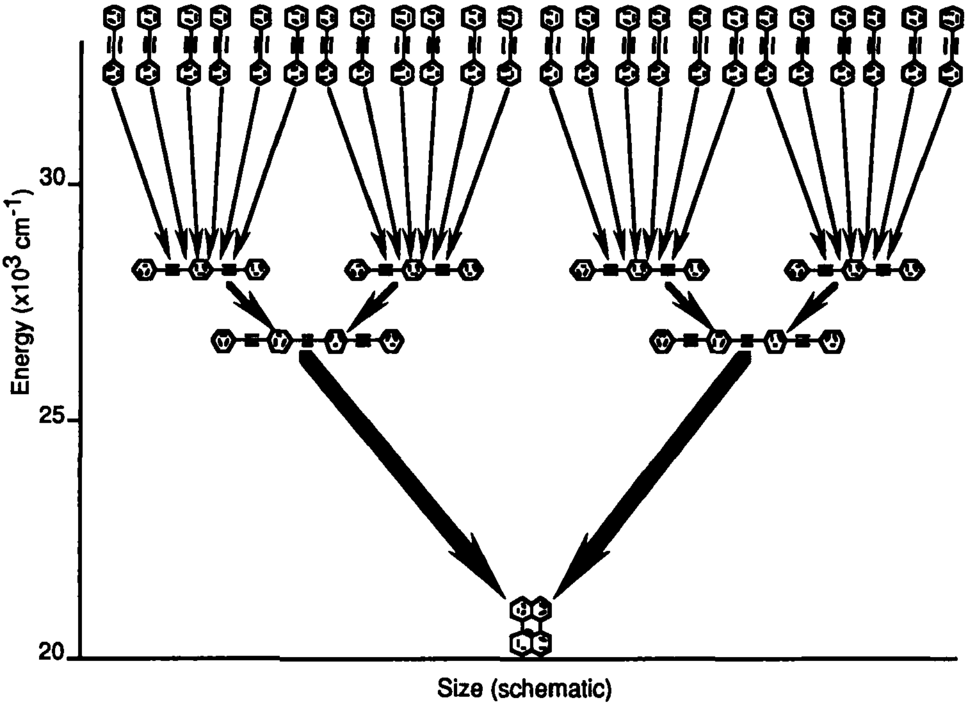

FIGURE 3 Energy funnel in nanostar supermolecule: The energy ladder is based on Figs 1 and 2. The spatial size is a rough estimate. The upper energy step consists of 24 localized energy sites, the next of 4, then 2 and finally the one very compact acceptor.

The excitation spectrum of a 1 : 1 dilute solution of isolated donor (silicon substituted monodendron, M39-Si) and isolated acceptor (1-ethynylperylene) reveals that the radiative donor to acceptor energy transfer is quite inefficient. The emission intensity of the M39-Si monodendron donor overwhelms that of the perylene acceptor for a 312 nm excitation wavelength. In contrast, the emission spectrum of the nanostar is dramatically different from that of an equimolar mixture of donor and acceptor. There is nearly a complete absence of emission from the nanostar's intramolecular donor (it is down by a factor of 60 or more, and what little is seen may be, at least in part, due to an impurity species, M39-Si dimer). In the nanostar molecule, the perylenic emission equals that of the parent monodendron (M39-Si) molecule emission in number of photons (but not wavelength), within an uncertainty of a few percent; that is, the nanostar's intramolecular energy transfer efficiency from its donor (monodendron) fragment to its acceptor (pendant) fragment is about unity! Additionally, the emission by the 1-ethynylperylene acceptor, when attached to the donor, is 600 times brighter than that of a solution of 1-ethynylperylene under the same conditions (solvent, molarity, excitation wavelength, etc.). In fact, even when the acceptor is excited directly into its most absorbing peak, its emission intensity is nearly three times smaller than when 312 nm excitation is used to excite the nanostar. Since energy transfer is less destructive to a molecule than direct excitation, we have both increased the quantum efficiency and the photostability of the perylenic chromophore[25].

Fig. 3 summarizes the energy funnel model for the nanostar: a.) counting diphenyl acetylene fragments or just acetylenic groups gives 24 single-chain (periphery) localized states, all at about 32,000 cm^{-1} (see Fig. 2); b.) 4 two-membered linear chain states at 28,400 cm^{-1}, each of which is collecting the energy from 6 periphery states; c.) 2 three-membered linear chain states at 26,500 cm^{-1}, each collecting the energy from 2 two-membered chain states; d.) one perylenic acceptor state at 21,000 cm^{-1}, collecting the energy from the two three-membered linear chain states. This is a "supertrap" state[26, 27].

The nanostar represents a new class of "designer" molecules, tailor made for single molecule light and exciton sources. We note that the large size (about 100 Å), high photo-stability and near-unity efficiency will allow these supermolecules to be used as "supertips" for optical nanoprobes and nanosensors[28], as exciton sources for scanning exciton microscopy[15] and possibly as material for organic light emitting diodes (LEDs).

ACKNOWLEDGMENT

We would like to thank Xhifu Xu and Jeff Moore for carrying out the synthesis. We acknowledge support from the National Science Foundation NSF grant DMR 9410709.

REFERENCES

1. S. E. Webber, *Chem. Rev.* **90**, 1469 (1990).
2. M. A. Fox, W. E. Jones, D. M. Watkins, *Chem. Eng. News*, 38 (1993).
3. R. Kopelman, *J. Phys. Chem.* **80**, 2191-2195 (1976).
4. V. S.-Y. Lin, S. G. DiMagno, M. J. Therien, *Science* **264**, 1105-1111 (1994).
5. M. N. Berberan-Santos, et al., *J. Phys. Chem.* **97**, 11376-11379 (1993).
6. K. Lieberman, S. Harush, A. Lewis, R. Kopelman, *Science* **247**, 59-61 (1990).
7. R. Kopelman, W. Tan, *Science* **262**, 1382-84 (1993).
8. D. Birnbaum, S. K. Kook, R. Kopelman, *J. Phys. Chem.* **97**, 3091-3094 (1993).
9. W. Tan, Z. Y. Shi, S. Smith, D. Birnbaum, R. Kopelman, *Science* **258**, 778-781 (1992).
10. W. Tan, Z.-Y. Shi, R. Kopelman, *Anal. Chem.* **64**, 2985-2990 (1992).

11. A. Lewis, et al., in *Optical Microscopy for Biology* B. Herman, K. Jacobson, Eds. (Wiley-Liss, New York, 1990) pp. 615-639.
12. A. Lewis, K. Lieberman, *Anal. Chem.* **63**, 625A (1991).
13. E. Betzig, J. K. Trautman, T. D. Harris, J. S. Weiner, R. L. Kostelak, *Science* **251**, 1468 (1991).
14. E. Betzig, J. K. Trautman, *Science* **257**, 189 (1992).
15. R. Kopelman, in *Physical and Chemical Mechanisms in Molecular Radiation Biology*, W. A. Glass, M. Varma, Eds. (Plenum Press, New York, 1991), vol. 58, pp. 475-502.
16. L. L. France, N. E. Geactinov, J. Breton, L. Valkunas, *Biochim. Biphys. Acta* **1101**, 105-119 (1992).
17. L. Valkunas, *J. Photochem. Photobiol. B: Biol.* **15**, 159-170 (1992).
18. L. Valkunas, N. E. Geactinov, L. L. France, *J. Lumin.* **51**, 67-78 (1992).
19. O. J. G. Somsen, F. v. Mourik, R. v. Grondelle, L. Valkunas, *Biophys. J.* **66**, 1-7 (1994).
20. A. H. Francis, R. Kopelman, in *Laser Spectroscopy of Solids* W. M. Yen, P. M. Selzer, Eds. (Springer-Verlag, Berlin, 1986), vol. 49, pp. 241.
21. Z. Xu, Z.-Y. Shi, W. Tan, R. Kopelman, J. S. Moore, *Polymer Preprints* **34**, 130-131 (1993).
22. Z. Xu, J. S. Moore, *Angew. Chem. Int. Ed. Engl.* **32**, 1354-1357 (1993).
23. R. Kopelman, *Rec. Chem. Progr.* **31**, 211-24 (1970).
24. S. T. Gentry, R. Kopelman, *J. Phys. Chem.* **88**, 3170-2 (1984).
25. This is again analogous to the photosynthetic system (17), where only one excitation at a time is transferred from the antenna to the reaction center.
26. R. Kopelman, in *Modern Problems in Condensed Matter Sciences* V. M. Agranovich, R. M. Hochstrasser, Eds. (North-Holland, Amsterdam, 1983), vol. 4, pp. 139-184.
27. S. T. Gentry, R. Kopelman, *Phys. Rev. B: Condens. Matter* **27**, 2579-82 (1983).
28. R. Kopelman, W. Tan, *Appl. Spec. Rev.* **29**, 39 (1994).