

Core, Shell, and Surface-Optimized Dendrimers for Blue Light-Emitting Diodes

Tianshi Qin,[†] Wolfgang Wiedemair,[‡] Sebastian Nau,[‡] Roman Trattnig,[‡] Stefan Sax,[‡] Stefanie Winkler,[§] Antje Vollmer,[§] Norbert Koch,^{§,⊥} Martin Baumgarten,[†] Emil J. W. List,^{*,‡,¶} and Klaus Müllen^{*,†}

⁺Max-Planck-Institut für Polymerforschung, D-55128 Mainz, Germany

*NanoTecCenter,,Weiz Forschungsgesellschaft mbH, A-8160 Weiz, Austria

[§]Helmholtz Zentrum Berlin für Materialien und Energie GmbH Elektronenspeicherring, D-12489 Berlin, Germany

[⊥]Institut für Physik, Humboldt-Universität zu Berlin, D-12489 Berlin, Germany

[¶]Institut für Festkörperphysik, Technische Universität Graz, A-8010 Graz, Austria

S Supporting Information

ABSTRACT: We present a novel core—shell—surface multifunctional structure for dendrimers using a blue fluorescent pyrene core with triphenylene dendrons and triphenylamine surface groups. We find efficient excitation energy transfer from the triphenylene shell to the pyrene core, substantially enhancing the quantum yield in solution and the solid state (4-fold) compared to dendrimers without a core emitter, while TPA groups facilitate the hole capturing and injection ability in the device applications. With a luminance of up to 1400 cd/m², a saturated blue emission CIE_{xy} = (0.15, 0.17) and high operational stability, these dendrimers belong to the best reported fluorescence-based blue-emitting organic molecules.

Reliable structure-property relationships and exceptional stability are mandatory for the commercialization of organic semiconductor devices,¹ which in particular qualifies dendrimers with their structural variability, as a promising class of macromolecules for such applications.² Recent progress in organic synthesis provides the buildup of dendritic macromolecules bearing functional building blocks in the core and the shell, and on the surface. Different from both small molecules and linear conjugated polymers, the stepwise generation-by-generation growth of dendrimers allows for the controlled synthesis of highly defined threedimensional shape-persistent dendritic structures incorporating subunits in defined positions.³ Thereby, it is possible to realize design concepts particularly optimized for "dendrimer light-emitting diodes" (DLEDs) relevant features, such as photoluminescence quantum yield (PLQY), exact emission color, overall stability, solubility, and the ability of charge capture and injection in the periphery.

Hence, we herein implemented all design aspects in the chosen core—shell—surface dendrimer (**PYGTPA**, Scheme 1) as follows: (i) the shape-persistence provides perfect site-definition of individual chromophore units as required for implementing a resonance energy transfer donor—acceptor system to boost the quantum yield and control the emission color at the same time;⁴ (ii) the spherical nature of the molecule provides a steric shield

Scheme 1. Synthesis Strategy toward Dendrimers PYGTPA, PYG2, and PYGCAP



^{*a*} Reagents and conditions: (a) *o*-xylene, 170 °C, microwave, 91% for **3**, 82% for **PYGTPA**, 84% for **PYG2**, 81% for **PYGCAP**; (b) TBAF, THF, RT, 88% for **4**.

for the central energy acceptor unit from which the emission will occu, thereby allowing the implementation of a wide range of emitter molecules; 5 (iii) suitable redox-active moieties on the surface enhance selective charge capturing and optimized carrier injection

Received:October 29, 2010Published:January 4, 2011

	solution		film				
	$\lambda_{ m em}$ nm	$\Phi_{ m PL}\%^b$	$\lambda_{ m em}$ nm	$\Phi_{ ext{PL}}^{**}$ rel.% ^c	$L_{\rm v}$ @8 V cd/m ²	$V_{\rm on}{\rm V}$	CIE, <i>x</i> , <i>y</i>
TPG2 ^a	410	27	431	100	300	6.0	0.19, 0.18
PYG2	456	74	469	324	1132	4.4	0.19, 0.27
PYGCAP	450	88	463	410	728	3.4	0.15, 0.18
PYGTPA	450	73	463	442	1443	3.2	0.15, 0.17
^a Taken from re	f 11. ^b Relative to	auinine sulfate deh	vdrate. ^{<i>c</i>} Relative	e to TPG2 as 100%.			

Table 1. Photophysical Properties and Device Performances of Dendrimers

from the electrode;⁶ (iv) the strongly twisted benzene rings of the dendrimer scaffold provide high solubility without the necessity of further side-chain substitution and thereby yield thermally stable amorphous thin films with high glass transition temperatures,⁷ also omitting alkyl chains as solubilizing side groups and thus enhancing the stability of devices.⁸

The divergent synthetic route toward a series of blue lightemitting dendrimers is shown in Scheme 1. The key first-generation dendrimer 4 was obtained in two steps from 1,3,6,8-tetraethynylpyrene 1 and 1,3-diphenyl-6,9-bis(triisopropylsilyl-ethynyl)cyclopentaphenanthrenone 2 by [4 + 2] Diels—Alder cycloaddition and TiPS desilylation in quantitative yields, and allowed the synthesis of different second-generation dendrimers (**PYGTPA**, **PYG2**, and **PYGCAP**) with various surface groups in good yields. All dendrimers are highly soluble in common organic solvents (~20 mg/mL in dichloromethane, THF, and toluene), and can thus be purified by column chromatography. The MALDI-TOF mass spectrum demonstrated that all dendrimers are monodisperse with their molecular weights being identical to the calculated masses (Figure S1, Supporting Information [SI]).

All substances have been analyzed for their optical properties in solution and in the solid state (Figures S2 and S3, SI). As summarized in Table 1 all **PYGx** dendrimers are characterized by an unstructured emission spectrum in the blue spectral region and an absorption band located in the UV. For all **PYGx** dendrimers the emission is stemming from the pyrene core as a consequence of an onging energy transfer.^{9,10} The efficient dipolar coupling of the core—shell triphenylene—pyrene system becomes in particular evident as one observes a drastically enhanced PLQY of all **PYGx** systems due to excitation energy transfer. A comparison reveals that **PYGx** show a PLQY improvement of up to 88% compared to 27% of previously reported **TPG2** in solution.¹¹ As a consequence of the shape persistent molecular design of **PYGx** dendrimers the relative PLQY in thin films was even improved 3-fold for **PYG2** and 4-fold for **PYGCAP** and **PYGTPA** as compared to **TPG2**.

To determine the absolute location of the energy levels of the **PYGx** dendrimers and the relative energy alignment of the core shell and surface groups, ultraviolet photoelectron spectroscopy (UPS) was performed (Figure S4, SI). The results show that (a) the energy levels of the pyrene core (HOMO = 5.7 eV; LUMO = 2.8 eV) are located within the band gap of the triphenylene (HOMO = 6.2 eV; LUMO = 2.8 eV) as required for energy transfer and (b) that adding the TPA groups on the surface in **PYGTPA** drastically reduces the injection barrier from the PEDOT:PSS electrode by ~0.65 eV compared to **PYG2** and **PYGCAP**; thus, **PYGTPA** represents indeed an optimized molecular core—shell—surface design for device applications. From UPS investigations on heterolayer structures PEDOT:PSS/**PYGx** 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBi) was chosen as the electron transport layer for devices. TPBi deposition onto



Figure 1. Voltage-current-luminance characteristics of PYGTPA DLED.

PYGx films lowered the sample work function by 0.2 eV (**PYG2** and **PYGTPA**) and 0.4 eV (**PYGCAP**) due to interface dipoles at the organic heterointerfaces.¹²

On the basis of these results a device configuration ITO/ PEDOT:PSS/**PYGx**(30 nm)/TPBi(10 nm)/CsF(8 nm)/Al was used to test the dendrimers in light-emitting devices. The key results for optimized devices using PYG2, PYGCAP, and PYGTPA are summarized in Table 1. For PYGTPA the best stability and highest luminance of 1440 cd/m^2 with a deep blue emission spectrum with $CIE_{xy} = (0.15, 0.17)$ and an overall efficiency of 0.26 cd/A was achieved (Figure 1). With these values the presented dendrimers possess the best brightness and stability values thus far reported for solution-processed saturated blue-emitting dendrimer-based devices.¹³ As compared to fluorescent poly(p-phenylene)-based blue-emitting materials, our results are comparable with respect to device brightness and stability for single-layer devices.14,15 This excellent material performance can be attributed to both the presented dendrimer design as well as the chosen synthetic concept, allowing for perfect site definition of the dendrimer.

In conclusion, the core—shell—surface design yields a dendrimer with high quantum yield and optimized charge injection properties and which, as a consequence of the shape-persistent molecular design, maintains all properties in the solid state. Furthermore, using a synthetic route based on noncatalytic Diels—Alder cycloaddition not only allows for a defined generation-bygeneration growth of the dendrimers yielding highly defined monodisperse molecular weight materials, which are free of unknown structural defects, but also completely rules out metal catalyst contamination and polymeric defects.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, MALDI-Mass, UV-vis, photoluminescence spectra, UPS, and

schematic energy level diagram. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

e.list@tugraz.at; muellen@mpip-mainz.mpg.de

ACKNOWLEDGMENT

This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG) within the frame of the Sonderforschungsbereich (SFB) 625. S.N. and S.S. acknowledge the financial support of POLYLED.

REFERENCES

(1) Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Shiyanovskaya, I.; Singer, K. D.; Balagurusamy, V. S. K.; Heiney, P. A.; Schnell, I.; Rapp, A.; Spiess, H. W.; Hudson, S. D.; Duan, H. *Nature* **2002**, *419*, 384–387.

(2) Lo, S. C.; Burn, P. L. Chem. Rev. 2007, 107, 1097–1116.

(3) Hecht, S.; Frechet, J. M. J. Angew. Chem., Int. Ed. 2001, 40, 74–91.

(4) Wang, J. L.; Yan, J.; Tang, Z. M.; Xiao, Q.; Ma, Y. G.; Pei, J. J. Am. Chem. Soc. 2008, 130, 9952–9962.

(5) Furuta, P.; Brooks, J.; Thompson, M. E.; Frechet, J. M. J. J. Am. Chem. Soc. 2003, 125, 13165–13172.

(6) Thelakkat, M. Macromol. Mater. Eng. 2002, 287, 442–461.

(7) Abbel, R.; Woffs, M.; Bovee, R. A. A.; van Dongen, J. L. J.; Lou,

X.; Henze, O.; Feast, W. J.; Meijer, E. W.; Schenning, A. Adv. Mater. 2009, 21, 597–602.

(8) Adronov, A.; Frechet, J. M. J. *Chem. Commun.* **2000**, *18*, 1701–1710.

(9) Markovitsi, D.; Germain, A.; Millie, P.; Lecuyer, P.; Gallos, L. K.; Argyrakis, P.; Bengs, H.; Ringsdorf, H. *J. Phys. Chem.* **1995**, *99*, 1005– 1017.

(10) Park, Y. H.; Rho, H. H.; Park, N. G.; Kim, Y. S. Curr. Appl. Phys. 2006, 6, 691–694.

(11) Qin, T. S.; Zhou, G.; Scheiber, H.; Bauer, R. E.; Baunigarten, M.; Anson, C. E.; List, E. J. W.; Mullen, K. *Angew. Chem., Int. Ed.* **2008**, 47, 8292–8296.

(12) Zhu, X. Y.; Kahn, A. MRS Bull. 2010, 35, 443-448.

(13) Burn, P. L.; Lo, S. C.; Samuel, I. D. W. Adv. Mater. 2007, 19, 1675-1688.

(14) Sax, S.; Rugen-Penkalla, N.; Neuhold, A.; Schuh, S.; Zojer, E.; List, E. J. W.; Mullen, K. *Adv. Mater.* **2010**, *22*, 2087–2091.

(15) Mitschke, U.; Bauerle, P. J. Mater. Chem. 2000, 10, 1471-1507.