CHEMISTRY
A EUROPEAN JOURNAL

ChemPubSoc Europe

DOI: 10.1002/chem.201300728

Synthesis of Highly Fluorescent Diquinaldinatoalumino Silole Derivatives

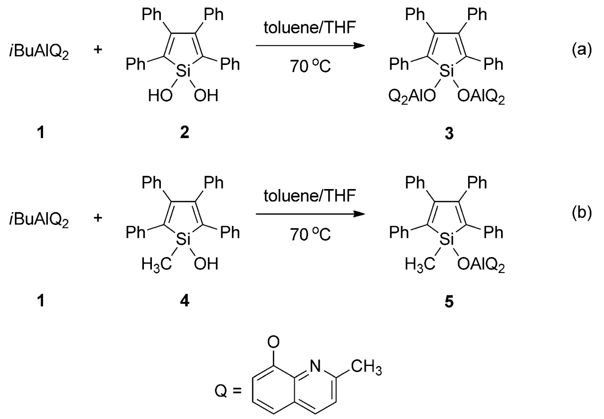
Erika Pusztai,[a] Seunghyun Jang,[a] Irina S. Toulokhonova,[a] Ilia A. Guzei,[a]
Robert West,*[a] Rongrong Hu,[b] and Ben Zhong Tang[b]

Silicon-containing π-conjugated compounds, especially siloles, have recently received significant attention because of their unusual optical and electronic properties.[1–4] In siloles, σ^*–π^* conjugation between the σ^* orbital of the silicon atom and the π^* orbital of the butadiene fragment leads to a low LUMO energy level and a small HOMO–LUMO gap. Siloles can be useful as electron-transporting materials in electronic devices,[5] including light-emitting diodes (LEDs).[6–8] Many silole derivatives have been obtained recently by simple chemical reactions,[9] but there are few attempts to develop silole derivatives displaying blue luminescence. Herein, we report the synthesis of two new highly fluorescent, blue emitting siloles with aluminoquinaldinate groups attached to the silicon atom.

Tris-(8-oxyquinolinato) aluminum (Alq_3) is a favored material for fabrication of electroluminescent devices as an electron transporter and emitter.[10–11] It is stable and emits green light with peak wavelength around $\lambda \approx 520$ nm with high quantum efficiency in the solid state. To shift the luminance of aluminum complex to the blue region, donor groups at the positions 2 or 4 of the 8-oxyquinoline ligand or acceptors at position 5 of the ligand have been introduced.[12,13] Tris-(2-methyl-8-oxyquinolinato) aluminum (AlQ_3) shows not only a significant blueshift on the UV and fluorescence spectra, but also increased fluorescence quantum yield efficiency in solution.[12] Because AlQ_3 is not stable in air, its stable derivative, (μ-oxo)-bis(bis(2-methyl-8-quinolinolato)-aluminum(III)) (Q_2Al-μO-AlQ_2), was also investigated, and it showed very similar optical properties.[14] Earlier work showed that replacing one 2-methyl-8-oxyquinoline in tris(2-methyl-8-oxyquinolinato)aluminum by a triphenylsiloxy substituent resulted in a slight blueshift of the emission maximum, but this compound displayed no increased emission efficiency.[15]

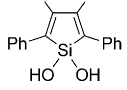
For high-performance OLEDs, a very large photoluminescence quantum yield is required.[16] To achieve this, doping of a highly fluorescent or phosphorescent molecule (guest) into an emitting layer (host) is the usual approach. However, doping complicates the fabrication process, and it would be ideal to synthesize a molecule with very high quantum efficiency and use it for fabrication of OLEDs without doping.

To increase the efficiency of fluorescence, we have designed a system, in which effective electron transport and emissive moieties are combined in one molecule, by attaching an aluminoquinaldinate complex to a silole group. In the reactions of *i*butylaluminodiquinaldinate, *i*$BuAlQ_2$ (**1**), with 1,1-dihydroxy-2,3,4,5-tetraphenylsilole (**2**), 1,1-bis(aluminodiquinaldinate)-2,3,4,5-tetraphenylsilole (**3**) was prepared as shown in Scheme 1a. In another reaction, *iso*-butylaluminodiquinaldinate, *i*$BuAlQ_2$ (**1**), with 1-methyl-1-hydroxy-2,3,4,5-tetraphenylsilole (**4**), 1-methyl-1-aluminodiquinaldinate-2,3,4,5-tetraphenylsilole (**5**) was prepared as shown in Scheme 1b.



Scheme 1. Synthetic route for the synthesis of 1,1-bis(diquinaldinatoalumino)silole (**3**) and 1-methyl-1-diquinaldinatoalumino silole (**5**).

The silole complexes **3** and **5** were identified by ^1H, ^{13}C, and ^{29}Si-NMR, X-ray crystallography, and mass spectra. The crystal structure of **3** is presented in Figure 1, whereas that of **5** is shown in Figure 2.



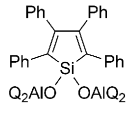
2

---

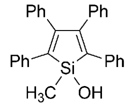
[a] E. Pusztai, Dr. S. Jang, Dr. I. S. Toulokhonova, Dr. I. A. Guzei,
Prof. R. West
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706 (USA)
E-mail: west@chem.wisc.edu

[b] Dr. R. Hu, Prof. B. Z. Tang
Department of Chemistry and
State Key Laboratory of Molecular Neuroscience
Institute of Molecular Functional Materials
The Hong Kong University of Science & Technology
Clear Water Bay, Kowloon, Hong Kong (P.R. China)

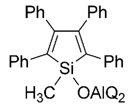
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201300728.



3



4



5

Q_2Al-μO-AlQ_2 exhibited an absorption band at $\lambda = 365$ nm, whereas Alq_3 has its characteristic absorption band at 395 nm, and a similar difference was observed in the fluorescence spectra, because Alq_3 emits at $\lambda = 517$ and Q_2Al-μO-AlQ_2 at 485 nm. Silole complex **3** exhibited UV absorption maxima at $\lambda = 258$ and at 365 nm, and silole complex **5**—at 258 and 370 nm, as shown in Figure 3. For comparison, 1,1-dimethyl-2,3,4,5-tetraphenylsilole and 1-methyl-1,2,3,4,5-pentaphenylsilole exhibited an absorption band at $\lambda = 360$ and 370 nm, respectively, due to a π–π* transition of the silole ring.[17,18] On this basis, we assigned the 365 and 370 nm bands to a similar π–π* transition of the silole group that overlaps with the absorption band of the 2-methyl-8-oxyquinaldinate.

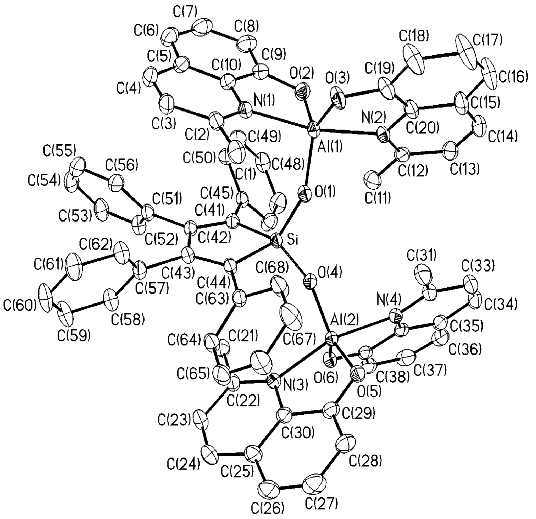


Figure 1. X-ray diffraction single-crystal structure of **3**. The displacement ellipsoids were drawn at the 50% probability level. All hydrogen atoms have been omitted for clarity.

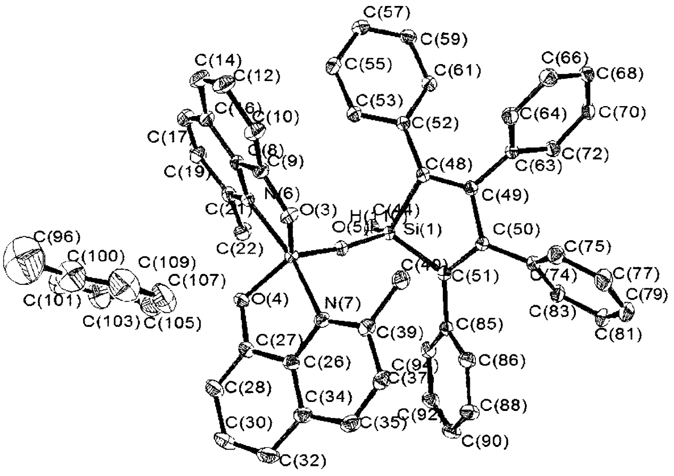


Figure 2. X-ray diffraction single-crystal structure of **5**. The displacement ellipsoids were drawn at the 50% probability level. All hydrogen atoms have been omitted for clarity.

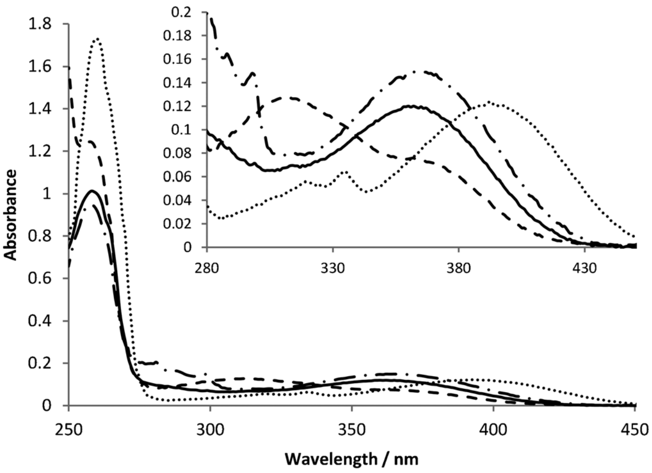


Figure 3. UV absorption spectra of **3** (——) and **5** (–•–•) compared to Alq_3 (••••) and Q_2Al-μO-AlQ_2 (-----); 10 ppm solutions in THF.

The fluorescence spectrum of quinaldinate complexes **3** and **5** are shown in Figure 4 (bottom). The emission band is a broad band centered at $\lambda_{em} = 478$ nm, strongly blueshifted compared to 1,1-dihydroxy-2,3,4,5-tetraphenylsilole (**2**; $\lambda = 520$ nm) and Alq_3 ($\lambda = 517$ nm, Figure 4, top). The blueshift of fluorescence in some pentacoordinated aluminoquinoli-

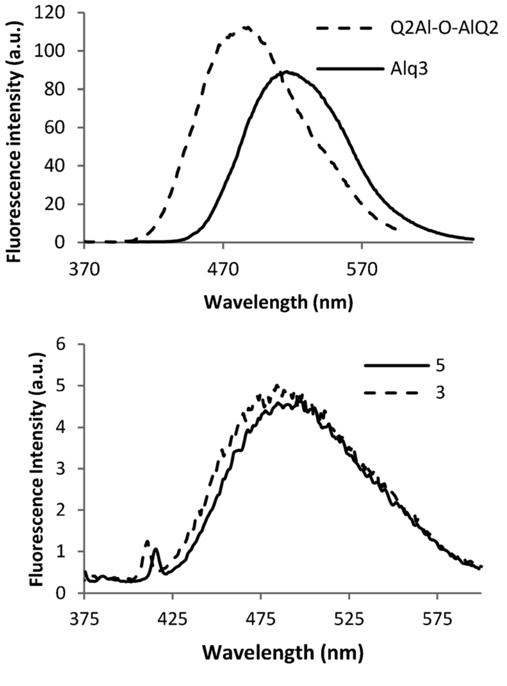


Figure 4. Fluorescence spectra of **3** (-----) and **5** (——) compared to Alq_3 (——) and Q_2Al-μO-AlQ_2 (-----); 10 ppm solutions in THF.

nates has been attributed to weakening of Al–N coordination bond in these complexes.[19] However, from our structural data for pentacoordinated aluminoquinolinate complexes,[20] we suggest that the blueshift may arise from a donor effect at the C-2. La Deda and co-workers calculated that shortening of the Al–O bond will increase energy gap between HOMO and LUMO of the 2-methylquinolin-8-olate chelants leading to blue emission.[21] Compounds **3** and **5** behave like new chromophores, which show the combined property of the quinaldinate and the silole moiety, but according to the shape and the emission maximum, silole might take a leading effect in this combined fluorescent behavior.[17,18]

Efficiency of emission was investigated in THF with quinine sulfate in H_2SO_4 (0.1 N) as a standard.[22] Silole complexes **3** and **5** exhibited low emission efficiency $<1\,\%$ in solution. The solid-state quantum yield was determined with an integrating sphere according to the method described by Mello et al.[23] Compound **3** displayed an extremely high quantum yield of 95 %, compared to 35 % for Alq_3, and 24 % of Q_2Al-μO-AlQ_2, but also **5** exhibited 81 % quantum yield.

Furthermore, light-emitting devices[24] with the structure ITO/NPB/**3**/TPBi/Alq_3/LiF/Al and ITO/NPB/**5**/TPBi/LiF/Al were fabricated (ITO = indium tin oxide; NPB = *N*,*N'*-bis(naphthalen-1-yl)-*N*,*N'*-bis(phenyl)benzidine; TPBi = 1,3,5-tris(*N*-phenylbenzimidazol) benzene). These devices emitted greenish-blue light at $\lambda = 520$ and 516 nm with the maximum luminance of 1770 and 5530 cd m^{-12}, respectively, at 15 V. Compound **5** showed especially good external quantum efficiency 2.75 % and outstanding current efficiency 7.89 cd A^{-1} (Table 1). Both devices had the onset voltage at 4.2 V. Details of the solid-state quantum yield and electroluminescence are described in the Supporting Information.

Table 1. Photophysical properties of silole complexes **3** and **5** compared to Alq_3 and Q_2Al-μO-AlQ_2.[a]

Complex	λ_{ab} [nm]	$\log \varepsilon$ [dm^3 mol^{-1} cm^{-1}]	λ_{em} [nm]	Φ_{Fsoln}	Φ_{Fsolid}
3	365	4.09 (4.08)	478	0.01	0.95
5	370	3.98	485	0.01	0.81
Q_2Al-μO-AlQ_2	365	3.66 (3.64)	485	0.24	0.24
Alq_3	395	3.77 (3.66)	520	0.11	0.35
quinine sulfate	347	3.70	445	0.54	–

[a] Abbreviations: λ_{ab} = absorption maximum in THF solution; ε = molar absorption coefficient at λ_{ab} and at 370 nm; λ_{em} = emission maximum in THF solution, Φ_{Fsoln} = fluorescence quantum yields in THF solution determined by using quinine sulfate in H_2SO_4 (0.1 N) as a standard. Φ_{Fsolid} = fluorescent quantum yield of solid powder determined by a calibrated integrating sphere.

In general, many conjugated organic emitters are highly emissive in dilute solution, but become weakly luminescent when fabricated into thin films due to aggregate formation in the solid state.[25] The molecules aggregate to form less emissive species, such as excimers, leading to a reduction in the luminescence efficiency.[26] However, since Tang and co-workers described the aggregation-induced emission (AIE) phenomena of siloles,[16] many silole derivatives have been found to exhibit unusual AIE properties.[27] We have also investigated the AIE of silole complexes **3** and **5** as shown in Figure 5. The concentration for **3** and **5** for the fluorescence measurements was 10 mg L^{-1} (10 ppm) in THF. Aggregate solutions were prepared by rapid injection of THF solutions containing **3** or **5** to water/THF solutions. Figure 5 b and d show plots for the relative PL intensity of silole complexes vs % water by volume. Silole-complex aggregates exhibited a nearly identical emission band, but were more strongly fluorescent than the non-aggregated silole complexes. The two complexes behave somewhat differently; for **3** aggregation begins at 60 % water concentration, whereas for **5** aggregation begins only at 80 % water and then rises exponentially. Probably, this difference reflects the lower steric hindrance and greater solubility of **5**.

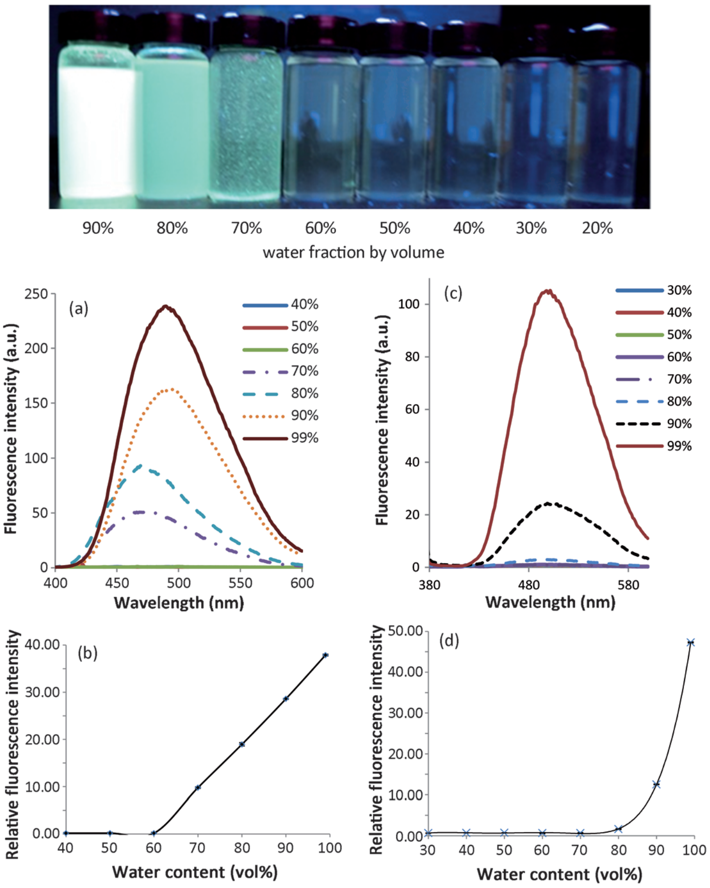


Figure 5. a) Fluorescence spectrum of **3** aggregates in water/THF mixtures and b) plot of the relative intensity of **3** aggregates versus vol % water. c) Fluorescence spectrum of **5** aggregates in water/THF mixtures and d) plot of the relative intensity of **5** aggregates versus vol % water.

In summary, two new highly fluorescent diquinaldinatoalumino silole complexes have been prepared. Combination of strong emitters and electron transporters, tetraphenylsilole and aluminoquinaldinate, in one molecule has led to a sky-blue emission with 2.7 fold increase of fluorescence efficiency in solid state compared to standard Alq_3. OLEDs with the structure of ITO/NPB/**3**/TPBi/Alq_3/LiF/Al and ITO/NPB/**5**/TPBi/LiF/Al were fabricated; they emit greenish-blue light at $\lambda = 520$ and 516 nm with luminance of 1770 and 5530 $cd\,m^{-12}$ at 15 V, respectively. Although further optimization will be needed, the silole–(O-AlQ_2)$_2$ compounds appear to be promising candidates for use in organic electronics.

Experimental Section

For detailed experimental procedures and characterization of products, see the Supporting Information. CCDC-913897 (**2**), CCDC-913895 (**3**), and CCDC-913896 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The authors thank Professor Hoi Sing Kwok and Yibin Jiang for providing technical support to the EL measurement, Haley Albright for the help at the syntheses, and the Rosztoczy Foundation for their support.

Keywords: aluminoquinaldinates · fluorescence · OLEDs · silicon · siloles

---

[1] R. West, H. Sohn, U. Bankwitz, J. Calabrese, Y. Apeloig, T. Mueller, *J. Am. Chem. Soc.* **1995**, *117*, 11608–11609.
[2] S. Yamaguchi, K. Tamao, *J. Chem. Soc. Dalton Trans.* **1998**, 3693–3702.
[3] S. Yamaguchi, T. Endo, M. Uchida, T. Izumizawa, K. Furukawa, K. Tamao, *Chem. Eur. J.* **2000**, *6*, 1683–1692.
[4] W. W. H. Wong, J. F. Hooper, A. B. Holmes, *Austral. J. Chem.* **2009**, *62*, 393.
[5] K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa, S. Yamaguchi, *J. Am. Chem. Soc.* **1996**, *118*, 11974–11975.
[6] H. Sohn, R. R. Huddleston, D. R. Powell, R. West, *J. Am. Chem. Soc.* **1999**, *121*, 2935–2936.
[7] Y. Xu, T. Fujino, H. Naito, T. Dohmaru, K. Oka, H. Sohn, R. West, *Jpn. J. Appl. Phys.* **1999**, *38*, 6915–6918.
[8] S. Yamaguchi, R. Z. Jin, K. Tamao, *J. Am. Chem. Soc.* **1999**, *121*, 2937–2938.
[9] a) J. Dubac, C. Guerin, P. Meunier in *The Chemistry of Organic Silicon Compounds, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, Chapter 34; b) K. Tamao, S. Yamaguchi, *Pure Appl. Chem.* **1996**, *68*, 139–144.
[10] C. W. Tang, S. A. Vanslyke, *Apply. Phys. Lett.* **1987**, *51*, 913–915.
[11] C. W. Tang, S. A. Vanslyke, C. H. Chen, *J. Appl. Phys.* **1989**, *65*, 3610–3616.
[12] M. Matsumura, T. Akai, *Jpn. J. Appl. Phys.* **1996**, *35*, 5357–5360.
[13] S. A. VanSlyke, P. S. Bryan, F. V. Lovecchio, U.S. Patent 5141671, **1992**.
[14] a) T. Iijima, T. Yamamoto, *J. Organomet. Chem.* **2006**, *691*, 5016–5023; b) S. A. VanSlyke, US Patent 5151629, **1992**.
[15] A. Misra, P. Kumar, S. K. Dhawan, M. N. Kamalasanan, S. Chandra, *Indian J. Pure Appl. Phys.* **2005**, *43*, 522–526.
[16] H. Murata, Z. H. Kafafi, M. Uchida, *Appl. Phys. Lett.* **2002**, *80*, 189–191.
[17] J. Luo, Z. Xie, J. W. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang, *Chem. Commun.* **2001**, 1740–1741.
[18] B. Z. Tang, X. Zhan, G. Yu, P. P. S. Lee, Y. Liu, D. Zhu, *J. Mater. Chem.* **2001**, *11*, 2974–2978.
[19] X. T. Tao, H. Suzuki, T. Wada, S. Miyata, H. Sasabe, *J. Am. Chem. Soc.* **1999**, *121*, 9447–9448.
[20] I. S. Toulokhonova, I. A. Guzei, M. Kavana, R. West, *Main Group Met. Chem.* **2002**, *25*, 489–495.
[21] M. La Deda, I. Aiello, A. Grisolia, M. Ghedini, M. Amati, F. Lelj, *Dalton Trans.* **2006**, 330–339.
[22] G. A. Crosby, J. N. Demas, *J. Phys. Chem.* **1971**, *75*, 991–1024.
[23] J. C. de Mello, H. F. Wittmannm, R. H. Friend, *Adv. Mater.* **1997**, *9*, 230–232.
[24] H. Y. Chen, W. Y. Lam, J. D. Luo, Y. L. Ho, B. Z. Tang, D. B. Zhu, M. Wong, H. S. Kwok, *Appl. Phys. Lett.* **2002**, *81*, 574–576.
[25] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121–128.
[26] S. A. Jenekhe, J. A. Osaheni, *Science* **1994**, *265*, 765–768.
[27] a) Y. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Soc. Rev.* **2011**, *40*, 5361–5388; b) W. Z. Wang, P. Lu, S. Chen, J. W. Y. Lam, Y. Liu, H. S. Kwok, Y. Ma, B. Z. Tang, *Adv. Mater.* **2010**, *22*, 2159–2163; c) M. Wang, G. Zhang, D. Zhang, D. Zhu, B. Z. Tang, *J. Mater. Chem.* **2010**, *20*, 1858–1867; d) J. Liu, Y. Zhong, J. W. Y. Lam, P. Lu, Y. Hong, Y. Yu, Y. Yue, M. Faisal, H. H. Y. Sung, I. D. Williams, K. S. Wong, B. Z. Tang, *Macromolecules* **2010**, *43*, 4921–4936; e) Z. Li, Y. Q. Dong, J. W. Y. Lam, J. Sun, A. Qin, M. Haussler, Y. P. Dong, H. H. Y. Sung, I. D. Williams, H. S. Kwok, B. Z. Tang, *Adv. Funct. Mater.* **2009**, *19*, 905–917; f) Z. Zhao, Z. Wang, P. Lu, C. Y. K. Chan, D. Liu, J. W. Y. H. Lam, H. Y. Sung, I. D. Williams, Y. Ma, B. Z. Tang, *Angew. Chem.* **2009**, *121*, 7744–7747; *Angew. Chem. Int. Ed.* **2009**, *48*, 7608–7611; g) J. L. Mullin, H. J. Tracy, J. R. Ford, S. R. Keenan, F. Fridman, *J. Inorg. Organomet. Polym. Mater.* **2007**, *17*, 201–213; h) S. Jang, S. G. Kim, D. Jung, H. Kwon, J. Song, S. Cho, Y. C. Ko, H. Sohn, *Bull. Korean Chem. Soc.* **2006**, *27*, 1965–1966; i) J. Chen, B. Xu, Y. Cao, *Synth. Met.* **2005**, *152*, 249–252.

Received: February 23, 2013