

Highly Efficient Photocatalytic Water Reduction with Robust Iridium(III) Photosensitizers Containing Arylsilyl Substituents**

Dong Ryeol Whang, Ken Sakai, and Soo Young Park*

As initiated by the pioneering studies of the Bernhard research group,^[1] enormous advances in cyclometalated Ir^{III} photosensitizers have been made in the pursuit of highly efficient visible-light-driven water-reduction systems.^[1–16] Many different classes of cationic Ir^{III} photosensitizers have been developed with the general structure [Ir^{III}(C[^]N)₂(N[^]N)]⁺, in which C[^]N is a monoanionic cyclometalating ligand and N[^]N is a neutral ancillary ligand.^[4] Photocatalytic water-reduction systems are typically benchmarked in terms of their turnover number (TON), which reflects the stability of the system under the operating conditions and is thus deeply related to the monetary expense for solar-to-hydrogen energy conversion.^[7] DiSalle and Bernhard designed a series of Ir^{III} photosensitizers with pendant pyridine moieties, which directed the adsorption of the complexes onto a colloidal platinum catalyst to generate H₂ with a TON value of 8800.^[5]

However, it has been shown that the overall photocatalytic performance of these systems is primarily limited by the fundamental degradation of photosensitizers during photolysis.^[11,12] Practically, the degradation of Ir^{III} photosensitizers has been suggested to occur by the water-assisted rupture of metal–N(N[^]N) bonds and subsequent solvolysis of the complex with the formation of solvento complexes.^[17,18] Some studies have shown that the stability of Ir^{III} photosensitizers can be improved I) by changing the organic cosolvent from acetonitrile (MeCN) to weakly coordinating tetrahydrofuran (THF),^[2] II) by introducing sterically bulky

alkyl groups on the N[^]N ligand,^[4] and III) by increasing the intrinsic stability of Ir^{III} photosensitizers by changing the framework from [Ir(C[^]N)₂(N[^]N)]⁺ (TON = 86) to [Ir(C[^]N[^]N)₂]⁺ (TON = 273).^[9]

In previous studies of light-emitting electrochemical cells, attempts were made to inhibit unwanted chemical reactions so that the fundamental inertness of cationic Ir^{III} complexes could be considerably improved. In this context, N[^]N ligands with bulky aromatic substituents, such as phenyl^[19,20] and Fréchet-type dendrons,^[21] were designed and tested. We believed that this approach could be applied to the improvement of photosensitizers for photocatalytic water reduction according to the above-mentioned strategy II.

We focus herein on the use of triphenylsilyl (TPS) groups as bulky moieties to prevent ligand substitution and thus further improve the inertness as well as the sensitivity of Ir^{III} photosensitizers. In our previous studies, TPS groups together with related groups were successfully attached to neutral Ir^{III} complexes to provide highly efficient organic light-emitting devices.^[22–24] These studies showed that arylsilyl groups, such as TPS groups, provide sufficient steric hindrance to protect typical reactive centers by imparting a so-called “site-isolation effect” to the chromophores.^[22–27] Herein we show that the three aryl rings around the silicon atom of TPS groups are remarkably efficient in protecting the complex from ligand substitution only if the groups are introduced at the N[^]N site. The enhanced stability of a series of TPS-containing Ir^{III} photosensitizers are examined in detail in conjunction with their actual photosensitization characteristics in the photoreduction of water.

A series of Ir^{III} photosensitizers with TPS substituents in various positions were designed and synthesized together with related control compounds (Scheme 1). Moreover, we employed two different C[^]N ligands, 2-(2,4-difluorophenyl)pyridine (dfppy) and 2-phenylpyridine (ppy), to tune the photophysical and electrochemical properties of the Ir^{III} photosensitizers. We also synthesized and examined an Ir^{III} photosensitizer with 4,4'-diphenyl-2,2'-bipyridine as the N[^]N ligand (Irbpbpy) to explore the relationship between substituent size and the photosensitizer performance. All Ir^{III} photosensitizers were synthesized according to standard procedures (see the Supporting Information).

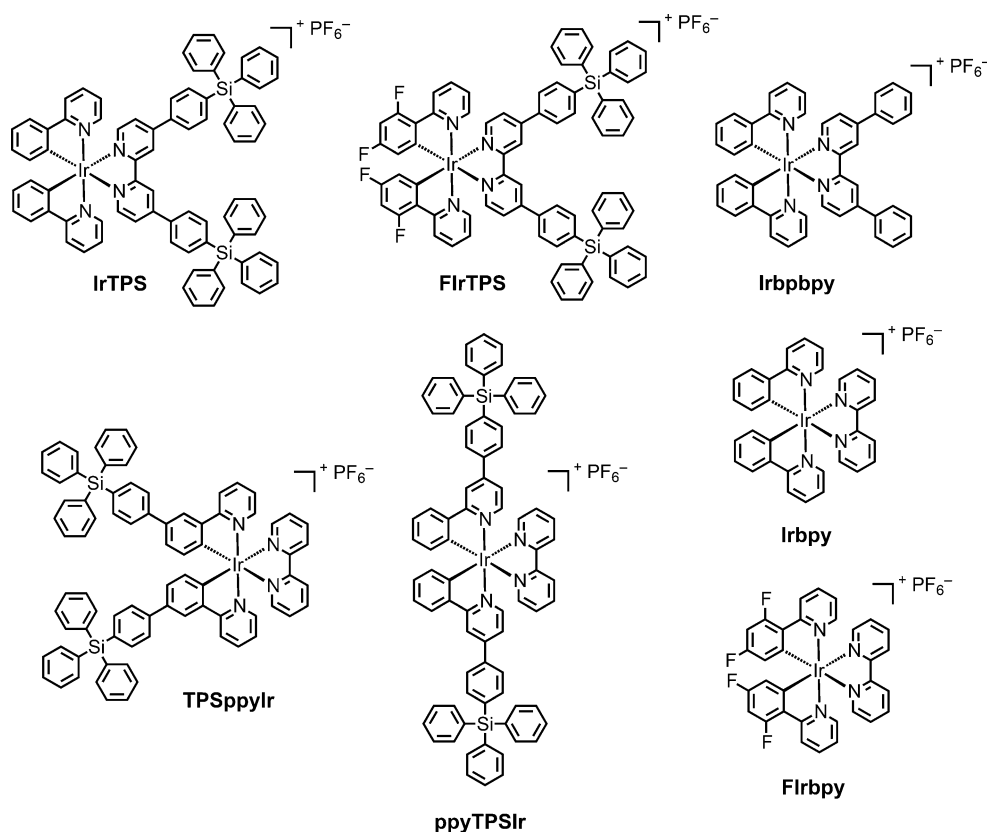
Photocatalytic water-reduction efficiency with the Ir^{III} photosensitizers was evaluated by visible-light irradiation ($\lambda > 400$ nm) of the system in cooperation with colloidal platinum as a water-reduction catalyst (WRC) and triethylamine (TEA) as a sacrificial reducing agent. All experiments were carried out until gas evolution ceased, and the total TON values of the Ir^{III} photosensitizers were calculated on the basis of the number of single-electron-transfer processes

[*] D. R. Whang, Prof. S. Y. Park
Center for Supramolecular Optoelectronic Materials
WCU Hybrid Materials Program and Department of Materials
Science and Engineering, Seoul National University
Seoul 151-744 (Korea)
E-mail: parksy@snu.ac.kr
Homepage: <http://csom.snu.ac.kr>

Prof. K. Sakai
Department of Chemistry, Faculty of Sciences, Kyushu University
Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581 (Japan)
and
International Institute for Carbon-Neutral Energy Research
(WPI-I²CNER), Kyushu University (Japan)
and
International Research Center for Molecular Systems (IRCMS)
Kyushu University (Japan)

[**] This research was supported by the National Research Foundation of Korea (NRF) through a grant funded by the Korean government (MSIP; No. 2009-0081571). The research at Kyushu University was supported by the International Institute for Carbon-Neutral Energy Research (WPI-I²CNER), sponsored by the World Premier International Research Center Initiative (WPI), MEXT (Japan).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201305684>.



Scheme 1. Chemical structures of the Ir^{III} photosensitizers studied.

(see Table 1). Figure 1 shows the kinetic traces of hydrogen evolution driven by the Ir^{III} photosensitizers. IrTPS and FIrTPS showed total TON values of 17000 and 10000, respectively. To the best of our knowledge, these are the highest TONs observed for water-reduction catalysis with Ir^{III} photosensitizers. The control Ir^{III} photosensitizers without TPS moieties, Irbbpy and FIrbbpy, showed total TON values of 530 and 480, respectively. The effect of the size of substituent groups on the photosensitizer activity can be rationalized by comparing the TON values of IrTPS, Irbbpy, and Irbbpy.

Table 1: Photophysical and photocatalytic properties of Ir^{III} photosensitizers.

Entry	$\lambda_{\text{PL}}^{[a,b]}$ [nm]	$\tau_{\text{av}}^{[a,c]}$ [μs]	$E_{\text{ox}}^{[d]}$ [V]	$E_{\text{red}}^{[d]}$ [V]	TON (t_{irr} [h]) ^[e]
IrTPS	605	0.47	1.11	−1.26	17000 (144)
FIrTPS	531	0.95	1.44	−1.17	10000 (116)
Irbbpy	601	0.41	1.16	−1.17	4100 (72)
TPSppyIr	608	0.22	1.07	−1.28	570 (24)
ppyTPS	590	0.44	1.12	−1.29	800 (24)
Irbbpy	589	0.42	1.10	−1.33	530 (24)
FIrbbpy	529	1.3	1.45	−1.23	480 (25)

[a] Value for a 10 μM solution of the photosensitizer in argon-saturated THF. [b] $\lambda_{\text{ex}} = 300$ nm. [c] $\lambda_{\text{ex}} = 377$ nm. [d] The oxidation and reduction potentials were determined by cyclic voltammetry (versus Ag⁺/Ag). [e] TON = $2n(\text{H}_2)/n(\text{photosensitizer})$, as calculated for reactions carried out under the experimental conditions described in the Supporting Information. t_{irr} is the irradiation time.

Although the TON of phenyl-substituted Irbbpy (4100) is higher than that of the unfunctionalized Ir^{III} photosensitizer Irbbpy (TON = 530), it is still much smaller than that of the Ir^{III} photosensitizer IrTPS with a bulkier substituent (TON = 17000). The use of bulkier substituent groups presumably minimizes the accessibility of the iridium center to the solvent and thus prevents undesired photoinduced solvolysis of the photosensitizer. Notably, the TON values of the Ir^{III} photosensitizers containing TPS groups in the cyclometalating ligands (C[^]N), that is, TPSppyIr and ppyTPS, were observed to be 570 and 800, respectively, which are much smaller than those of IrTPS and FIrTPS. Thus, the introduction of TPS substituents on the N[^]N ligand resulted in a dramatic improvement in the stability

of the photosensitizer, whereas TPS substituents on the C[^]N ligands did not provide any stabilizing effect at all. This observation clearly indicates that the stability of these Ir^{III} photosensitizers is fundamentally governed by the inertness

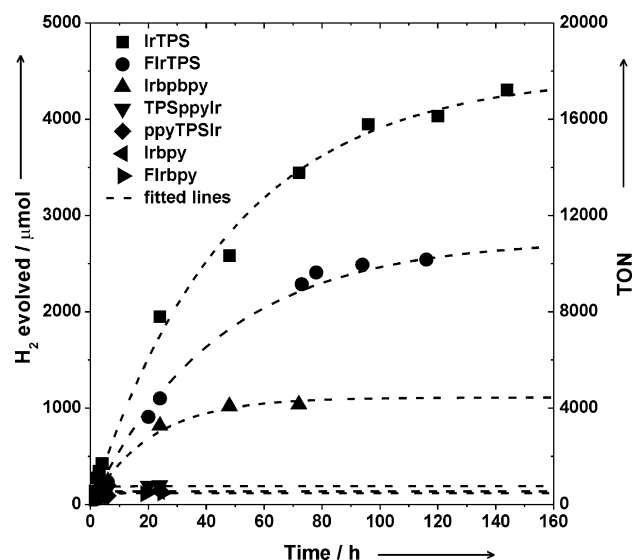


Figure 1. Kinetic traces of hydrogen evolution. A mixture of the Ir^{III} photosensitizer (0.50 μmol), K₂[PtCl₄] (0.50 μmol), TEA (1 mL), H₂O (1 mL), and THF (8 mL) in a 40 mL air-tight vial was irradiated with a 150 W Xe lamp with an interference filter that eliminated UV light of wavelengths below 400 nm. Fitted curves are shown with dashed lines.

of the N[^]N chelate during the light-induced events. As mentioned above, one possible interpretation is that ligand substitution of the N[^]N chelate is considerably retarded by the presence of bulky/protective TPS substituents, as substitution of the N[^]N ligand is likely to proceed by the so-called interchange associative mechanism.^[4,19–21] When the transition state for this substitution is reached, the reorganization energy required to relocate or twist the leaving bipyridyl chelate must be substantially larger when relatively large substituents, such as TPS groups, are tethered to the N[^]N ligand. This mechanism rationalizes well the higher stability of compounds with TPS moieties on the N[^]N ligand.

To confirm whether the high performance of IrTPS and FIrTPS was due to their intrinsic photochemical stability, we investigated the degradation of the photosensitizer itself in the absence of the sacrificial reagent and the WRC. Each sample containing IrTPS or Irbpy (50 μM) in THF and H₂O (9:1 v/v) was irradiated with visible light (λ > 400 nm), and the absorption spectral changes in the UV/Vis range were recorded (Figure 2; see the Supporting Information for other Ir^{III} photosensitizers). Whereas changes in the absorp-

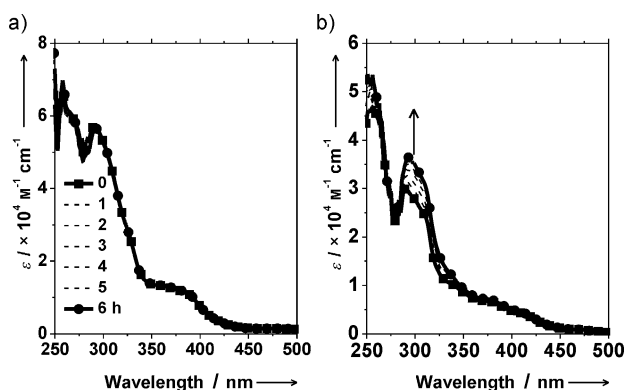


Figure 2. Absorption spectra of a) IrTPS and b) Irbpy at various time intervals during photoirradiation. In each case, a mixture of the Ir^{III} photosensitizer (50 μM) in THF and H₂O (9:1 v/v) was irradiated with a 150 W Xe lamp with an interference filter that eliminated UV light of wavelengths below 400 nm.

tion spectra of bpy- and bpbpy-bearing Ir^{III} photosensitizers clearly showed degradation upon photoirradiation, the spectra of IrTPS and FIrTPS barely changed. Thus, IrTPS and FIrTPS demonstrated outstanding photochemical stability. The increase in absorbance at around 300 nm upon photodegradation was assigned to the π–π* transition of the N[^]N ligand by comparison with the spectral features of free bpy and bpbpy (see Figure S2 in the Supporting Information); thus, this increase is due to the formation of free NN species upon the photodegradation of the Ir^{III} photosensitizers. These results clearly indicate that the Ir^{III} photosensitizers with phenyl groups on the N[^]N ligand (bpbpy) or TPS groups on the C[^]N ligands are rather susceptible to water-assisted solvolysis, in good agreement with the observed trend in the TON values for water-reduction catalysis, and further support our conclusion that the introduction of TPS substituents on the N[^]N ligand plays a crucial role in the dramatic stabiliza-

tion of the [Ir^{III}(C[^]N)₂(N[^]N)]⁺ framework. To ascertain the termination mechanism of the IrTPS-containing water-reduction system, we also checked the long-term stability (up to 120 h) of IrTPS and colloidal platinum (see the Supporting Information for a discussion).

To further ascertain the role of TPS substituents, we explored the photophysical and electrochemical properties of the Ir^{III} photosensitizers (Table 1). All synthesized Ir^{III} photosensitizers were found to be luminescent in THF. The photoluminescence (PL) energies and lifetimes of the Ir^{III} photosensitizers are primarily governed by the chemical structure of their parent C[^]N ligand (Table 1). The PL spectra of Ir^{III} photosensitizers incorporating ppy-based C[^]N ligands (IrTPS, Irbpbpy, TPSppyIr, ppyTPS^{Ir}, and Irbpy) are characterized by their emission maximum at 589–608 nm, whereas photosensitizers incorporating dfppy-based C[^]N ligands (FIrTPS and FIrbpy) showed an emission maximum at 529–531 nm. A similar trend was recognized in the PL lifetimes of ppy-based (τ_{av} = 0.22–0.47 μs) and dfppy-based Ir^{III} photosensitizers (τ_{av} = 0.95–1.3 μs). This trend is consistent with the electrochemical properties of the Ir^{III} photosensitizers. The first reduction potentials of all the Ir^{III} photosensitizers are virtually identical (E_{red} = –1.17––1.33 V) and are characteristic of bpy-centered reduction. On the other hand, the oxidation potentials are governed by the parent C[^]N ligand (Table 1, E_{ox} = 1.07–1.12 V for ppy-based Ir^{III} photosensitizers and E_{ox} = 1.44–1.45 V for dfppy-based Ir^{III} photosensitizers), in agreement with the fact that the electronic states of the Ir^{III} photosensitizers are largely governed by the parent C[^]N ligand with a minimal contribution from the TPS or phenyl substituents.

The above photophysical properties of the Ir^{III} photosensitizers can be rationalized by the results of DFT calculations. In both systems containing TPS-substituted bipyridyl ligands, no hybridization is observed between the phenyl rings of the TPS groups and the parent bipyridyl system. Thus, the electronic effects of TPS are limited to effects on the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the Ir^{III} photosensitizers. Figure 3 displays the optimized geometry of IrTPS and the HOMO/LUMO contour diagrams, which show negligible contributions of TPS to these frontier orbitals. Mulliken population analysis (MPA) revealed that the contributions of TPS fragments to the HOMO and LUMO are 0.01 and 0.63 %, respectively. Similar results were

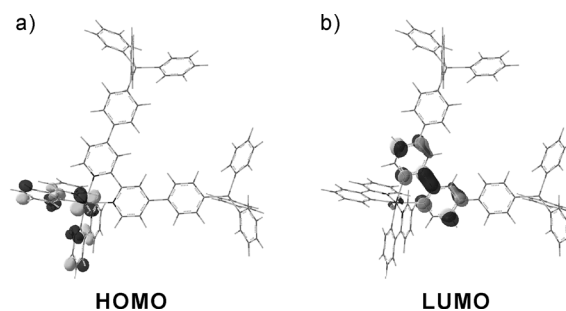


Figure 3. HOMO and LUMO isosurface plots for IrTPS. An isodensity value of 0.05 e Å^{–3} was applied for plotting the surfaces.

found for other TPS-containing Ir^{III} photosensitizers (see the Supporting Information). We can therefore conclude that the significant effects of TPS groups on the photochemical stability and TON of Ir^{III} photosensitizers are indeed caused by steric factors rather than electronic factors.

In this study, we successfully synthesized a series of [Ir^{III}(C[^]N)₂(N[^]N)]⁺ complexes with bulky/protective TPS substituent groups with the aim of developing new photocatalytic water-reduction systems with highly improved durability. Systematic exploration of the role of the TPS substituents revealed that the photosensitizers containing TPS groups at the N[^]N ligand exhibited dramatically enhanced durability. More importantly, the use of TPS groups led to the observation of exceedingly high TON values: the highest TON found was 17000 and thus the highest value reported to date. We believe that the results of this study indicate important new strategies for the design of more durable systems in various areas of photochemistry.

Received: July 2, 2013

Published online: September 10, 2013

Keywords: hydrogen production · iridium · photocatalysis · photosensitizers · water reduction

- [1] M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras, S. Bernhard, *Chem. Mater.* **2005**, *17*, 5712–5719.
- [2] E. D. Cline, S. E. Adamson, S. Bernhard, *Inorg. Chem.* **2008**, *47*, 10378–10388.
- [3] E. D. Cline, S. Bernhard, *Chimia* **2009**, *63*, 709–713.
- [4] P. N. Curtin, L. L. Tinker, C. M. Burgess, E. D. Cline, S. Bernhard, *Inorg. Chem.* **2009**, *48*, 10498–10506.
- [5] B. F. DiSalle, S. Bernhard, *J. Am. Chem. Soc.* **2011**, *133*, 11819–11821.
- [6] J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson, S. Bernhard, *J. Am. Chem. Soc.* **2005**, *127*, 7502–7510.
- [7] N. D. McDaniel, S. Bernhard, *Dalton Trans.* **2010**, *39*, 10021–10030.
- [8] S. Metz, S. Bernhard, *Chem. Commun.* **2010**, *46*, 7551–7553.
- [9] L. L. Tinker, S. Bernhard, *Inorg. Chem.* **2009**, *48*, 10507–10511.
- [10] L. L. Tinker, N. D. McDaniel, S. Bernhard, *J. Mater. Chem.* **2009**, *19*, 3328–3337.
- [11] L. L. Tinker, N. D. McDaniel, P. N. Curtin, C. K. Smith, M. J. Ireland, S. Bernhard, *Chem. Eur. J.* **2007**, *13*, 8726–8732.
- [12] F. Gärtner, A. Boddien, E. Barsch, K. Fumino, S. Losse, H. Junge, D. Hollmann, A. Bruckner, R. Ludwig, M. Beller, *Chem. Eur. J.* **2011**, *17*, 6425–6436.
- [13] F. Gärtner, D. Cozzula, S. Losse, A. Boddien, G. Anilkumar, H. Junge, T. Schulz, N. Marquet, A. Spannenberg, S. Gladiali, M. Beller, *Chem. Eur. J.* **2011**, *17*, 6998–7006.
- [14] F. Gärtner, S. Denurra, S. Losse, A. Neubauer, A. Boddien, A. Gopinathan, A. Spannenberg, H. Junge, S. Lochbrunner, M. Blug, S. Hoch, J. Busse, S. Gladiali, M. Beller, *Chem. Eur. J.* **2012**, *18*, 3220–3225.
- [15] F. Gärtner, B. Sundararaju, A. E. Surkus, A. Boddien, B. Loges, H. Junge, P. H. Dixneuf, M. Beller, *Angew. Chem.* **2009**, *121*, 10147–10150; *Angew. Chem. Int. Ed.* **2009**, *48*, 9962–9965.
- [16] D. Hollmann, F. Gärtner, R. Ludwig, E. Barsch, H. Junge, M. Blug, S. Hoch, M. Beller, A. Bruckner, *Angew. Chem.* **2011**, *123*, 10429–10433; *Angew. Chem. Int. Ed.* **2011**, *50*, 10246–10250.
- [17] E. Baranoff, B. F. E. Curchod, J. Frey, R. Scopelliti, F. Kessler, I. Tavernelli, U. Rothlisberger, M. Grätzel, M. K. Nazeeruddin, *Inorg. Chem.* **2012**, *51*, 215–224.
- [18] R. D. Costa, E. Ortí, H. J. Bolink, S. Graber, S. Schaffner, M. Neuburger, C. E. Housecroft, E. C. Constable, *Adv. Funct. Mater.* **2009**, *19*, 3456–3463.
- [19] H. J. Bolink, L. Cappelli, E. Coronado, M. Grätzel, E. Ortí, R. D. Costa, P. M. Viruela, M. K. Nazeeruddin, *J. Am. Chem. Soc.* **2006**, *128*, 14786–14787.
- [20] R. D. Costa, E. Ortí, D. Tordera, A. Pertegás, H. J. Bolink, S. Graber, C. E. Housecroft, L. Sachno, M. Neuburger, E. C. Constable, *Adv. Energy Mater.* **2011**, *1*, 282–290.
- [21] R. D. Costa, E. Ortí, H. J. Bolink, S. Graber, C. E. Housecroft, E. C. Constable, *Adv. Funct. Mater.* **2010**, *20*, 1511–1520.
- [22] J. J. Kim, Y. You, Y.-S. Park, J.-J. Kim, S. Y. Park, *J. Mater. Chem.* **2009**, *19*, 8347–8359.
- [23] Y. You, C. G. An, J. J. Kim, S. Y. Park, *J. Org. Chem.* **2007**, *72*, 6241–6246.
- [24] Y. You, C.-G. An, D.-S. Lee, J.-J. Kim, S. Y. Park, *J. Mater. Chem.* **2006**, *16*, 4706–4713.
- [25] R. J. Holmes, B. W. D'Andrade, S. R. Forrest, X. Ren, J. Li, M. E. Thompson, *Appl. Phys. Lett.* **2003**, *83*, 3818–3820.
- [26] X. Ren, J. Li, R. J. Holmes, P. I. Djurovich, S. R. Forrest, M. E. Thompson, *Chem. Mater.* **2004**, *16*, 4743–4747.
- [27] P.-I. Shih, C.-H. Chien, C.-Y. Chuang, C.-F. Shu, C.-H. Yang, J.-H. Chen, Y. Chi, *J. Mater. Chem.* **2007**, *17*, 1692–1698.