Molecular Engineering of Organic Sensitizers with Planar Bridging Units for Efficient Dye-Sensitized Solar Cells

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Dye-sensitized solar cells (DSSCs) have received a great deal of attention as low-cost alternatives to conventional pn junction solar cells.^[1] In these cells, the sensitizer is the key component. Although several Ru^{II} polypyridyl complexes exhibited high efficiencies above 10% and long-term stability,^[2-4] they are quite expensive and hard to purify. Recently, the performance of solar cells based on organic sensitizers has been remarkably improved, resulting in impressive efficiencies in the range of 8-10%.^[4] However, one of the drawbacks of organic sensitizers is the sharp and narrow absorption bands of their UV spectra in the blue region, impairing their light-absorption capabilities. Therefore, molecular engineering of organic sensitizers is required in order to broaden and redshift their absorption spectra. A successful approach was achieved through structural modification of the bridged unit.^[5] The introduction of a planar π -conjugated unit in the bridged framework is presumed to be the reason for the increase in the spectral response in the red region of the solar spectrum.^[6] Although organic-dye-based cells using an I^-/I_3^- electrolyte have afforded high power conversion efficiencies, recent studies on replacing the conventional I^-/I_3^- electrolyte with a Co^{II}/Co^{III} electrolyte have received renewed attention.^[7] Recently, Yella et al.^[8] reported an efficiency of 12.3% by using a Co^{II}/Co^{III} electrolyte in

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conjunction with a porphyrin sensitizer. While high conversion efficiency of 9-10% has been reached with organic sensitizers and porphyrin dyes using a liquid electrolyte, such as I^{-}/I_{3}^{-} or Co^{II}/Co^{III} redox couple, the stability issue still remains a major challenge due to leakage and evaporation. Accordingly, extensive studies have been conducted to substitute liquid electrolytes with quasi-solid-state or solid-state electrolytes. Herein, we report meticulously designed organic sensitizers incorporating a planar indeno[1,2-b]thiophene or indeno[1,2-b]thieno[2,3-d]thiophene bridging unit to understand the structure-property relationship (Scheme 1). We also investigate the photovoltaic performance of dyes using I^{-}/I_{3}^{-} , Co^{II}/Co^{III} , polymer gel, and solid-state electrolytes.



Scheme 1. Structure of JK-302, JK-303, and JK-304.

Scheme 2 illustrates the synthetic protocol for organic sensitizers JK-302, JK-303, and JK-304. The fluorenyl aminethiophene derivatives were synthesized by the Suzuki coupling^[9] of **1** with 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2dioxaborolane. The thiophene derivatives 2 were converted to their corresponding carbaldehydes 3 according to the Vilsmeier-Haack reaction.^[10] The aldehydes 3, upon reaction with cyanoacetic acid in the presence of piperidine, produced the sensitizers.

The visible absorption spectrum of JK-303 (Figure 1, Table S1 in the Supporting Information) exhibits two maxima at 368 and 491 nm, which are assigned as the π - π

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Scheme 2. Synthesis of JK-302, JK-303, and JK-304.



Figure 1. Left: absorption spectra of **JK-302**, **JK-303**, and **JK-304** in EtOH (solid lines) and TiO_2 film (dashed lines). Right: the emission spectra (dotted line) were obtained using the same solution by exciting at 462, 491, and 493 nm for **JK-302**, **JK-303**, and **JK-304**, respectively, at 298 K.

transitions of the conjugated molecule. The absorption band at 491 nm is significantly redshifted and broadened compared to that of the **JK-302** sensitizer. This observation can be readily interpreted by the more planar configuration in **JK-303**, which possesses a 1.7° twist between the indenothiophene and the thienyl unit, as compared with the more twisted one in **JK-302**, which has dihedral angles between the aniline and the thienyl unit and two thienyl units of 21.9 and 2.1°, respectively. A broader UV spectrum in **JK-304** relative to **JK-303** is derived from an increased delocalization over a bridged unit. The oxidation potential (Figure S1 in the Supporting Information) of 0.91 V in **JK-303** is more negative than that of 0.95 V in **JK-302**, reflecting the increased electron-donating nature, as compared to that of



JK-302, due to the delocalization of the π -conjugation system on the bridged unit. The excited-state oxidation potentials (E_{ox}^*) of three dyes are much more negative than the conduction band edge of TiO₂ at approximately -0.5 V versus NHE (NHE = normal hydrogen electrode), ensuring there is enough of a driving force for electron injection.^[11]

The molecular orbital calculations (Figure S7 in the Supporting Information) illustrate that the HOMOs are localized over the fluorenylamine and the LUMOs are localized over the cyanoacrylic acid, with a sizable population of the next thiophene unit. The examination of the HOMO–LUMO calculations indicates that the HOMO–LUMO excitation moves the electron distribution from the fluorenylamine to the cyanoacrylic acid, thus allowing a facile, photo-induced electron transfer from the dye to the TiO₂ electrode.

The photovoltaic performance of the devices composed of dyes in conjunction with an I^{-}/I_{3}^{-} electrolyte were obtained using an electrolyte comprising 1,2-dimethyl-3-propylimidazolium iodide (DMPImI, 0.6 M), I_2 (0.05 M), LiI (0.1 M), and *tert*-butyl pyridine (TBP, 0.8 M) in MeCN (Figure 2). The incident-photon-to-current conversion efficiency (IPCE) of **JK-303** (inset of Figure 2) exceeds 70 % in a broad spectrum range from 390 to 620 nm, reaching its maximum of 83 % at



Figure 2. J-V curve and IPCE spectra (inset) of **JK-302**, **JK-303**, and **JK-304**. Cell area tested with a metal mask: 0.16 cm².

515 nm. The IPCE spectrum of **JK-303** is much broader and red-shifted, as compared to that of **JK-302**, due to its extension of the π -conjugation and planar configuration, which is consistent with its absorption spectrum. Under AM 1.5G solar conditions (where AM = air mass and G = global), the **JK-303**-based solar cell exhibited a short-circuit current density (J_{sc}) of 15.40 mA cm⁻², an open-circuit voltage (V_{oc}) of 0.75 V, and a fill factor (*ff*) of 0.75, affording an overall efficiency of 8.69%. The integration of the incident-photon-to-current conversion efficiency curve under AM 1.5G conditions gave a J_{sc} of 15.31 mA cm⁻², which is in good agree-

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ment with the measured value. Under same conditions, an efficiency of 7.11% for a **JK-302**-sensitized cell ($J_{sc} = 12.97$ mA cm⁻²; $V_{oc} = 0.74$ V; ff=0.74) was obtained. A significant $J_{\rm sc}$ enhancement of **JK-303** and **JK-304** relative to that of JK-302 arises from the broad and redshifted absorption bands relative to JK-302.

To compare the performance of I^-/I_3^- with that of the Co^{II}/Co^{III} electrolyte, devices were fabricated with a Co^{II}/ Co^{III} electrolyte containing $[Co(bpy)_3](B(CN)_4)_2$ (0.22 M), $[Co(bpy)_3](B(CN)_4)_3$ (0.05 M), LiClO₄ (0.1 M), and TBP (0.8 M) in MeCN. A high conversion efficiency of 9.30% was achieved under simulated AM 1.5G solar conditions with JK-304 (Figures S8c and S9b in the Supporting Information) with a $J_{\rm sc}$ of 16.13 mA cm⁻², $V_{\rm oc}$ of 0.79 V, and ff of 0.73. This clearly outperforms the device based on the I^-/I_3^- electrolyte. The efficiency enhancement is primarily due to an increase in $J_{\rm sc}$ (ca. 0.40 mA cm⁻²) and $V_{\rm oc}$ (ca. 0.05 V). Similar trends have been observed for other dyes. From the photovoltaic performances measured under different illumination conditions (Table 1), one can see that impressive power

Table 1. J-V characterization of the DSSCs.

Electrolyte	$P_{\rm in} [{\rm mW}{\rm cm}^{-2}]$	$J_{\rm sc} [{ m mA}{ m cm}^{-2}]$	$V_{ m oc} \left[{ m V} ight]$	ff	$\eta \ [\%]^{[a]}$
JK-302					
iodine ^[b]	100.00	12.97	0.74	0.74	7.11
cobalt ^[c]	100.00	14.50	0.76	0.74	8.16
	50.10	7.91	0.73	0.72	8.31
	10.24	1.64	0.68	0.69	7.64
JK-303					
iodine ^[b]	100.00	15.40	0.75	0.75	8.69
cobalt ^[c]	100.00	15.74	0.78	0.77	9.04
	50.10	8.43	0.75	0.76	9.68
	10.24	1.82	0.69	0.75	9.44
JK-304					
iodine ^[b]	100.00	15.74	0.74	0.74	8.54
cobalt ^[c]	100.00	16.13	0.79	0.73	9.30
	50.10	8.88	0.77	0.74	10.24
	10.24	1.89	0.73	0.75	10.34

[a] Performances of DSSCs were measured with a 0.16 cm² metal mask. [b] Iodine-based electrolyte: DMPImI (0.6м), I₂ (0.05м), LiI (0.1м), TBP (0.8 M) in MeCN. [c] Cobalt-based electrolyte: [Co(bpy)₃](B(CN)₄)₂ (0.22 M), $[Co(bpy)_3]$ $(B(CN)_4)_3$ (0.05 M), $LiClO_4$ (0.1 M), and TBP (0.8 M)in MeCN.

conversion efficiencies over 10% under weak light irradiation have been achieved with JK-304. These are some of the highest values reported for DSSCs with a cobalt-based electrolyte.^[7]

Although highly efficient (over 10%) DSSCs have been achieved using a liquid electrolyte containing the Co^{II}/Co^{III} redox couple, the intrinsic drawbacks of liquid electrolytes, such as leakage and evaporation of the solvents, make it necessary to replace the liquid with polymer or hole-transporting materials (HTMs). In this study, the photovoltaic performance of the DSSCs was obtained using a polymer gel electrolyte containing DMPImI (0.6 M), I₂ (0.05 M), LiI (0.1 M), N-methylbenzimidazole (NMBI, 0.8 M), and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, 5 wt%) in MeCN. The JK-303-sensitized cell based on the polymer gel electrolyte under AM 1.5G solar conditions (Figure S10 and Table S2 in the Supporting Information) gave a $J_{\rm sc}$ of 14.39 mA cm⁻², a $V_{\rm oc}$ of 0.71 V, and a ff of 0.71, affording a conversion efficiency of 7.27%. This efficiency is one of the highest values based on organic sensitizers.^[12]

Iodine-free solid-state dye-sensitized solar cells (ssDSSCs) with poly(3,4-ethylenedioxythiophene) (PEDOT) as HTMs were fabricated through in situ solid-state polymerization of a brominated 3,4-ethylenedioxythiophene inside JK-303 or JK-304 adsorbed on TiO₂ nanopores. The photovoltaic performances (Figure 3) of the device are sensitive to the struc-



Figure 3. J-V curve and IPCE spectra (inset) of iodine-free ssDSSCs with JK-303 and JK-304 at 100 mW cm⁻². Cell area tested with a metal mask: 0.16 cm².

ture of the sensitizers. Importantly, both cells obtained high power conversion efficiencies compared with the N719based iodine-free ssDSSCs.^[13] In particular, the efficiency of 5.82% (Table S3 in the Supporting Information) for the JK-303-based iodine-free ssDSSCs is remarkable and is the highest value among the iodine-free ssDSSCs with PEDOT as the HTM.

To further study the electron transport and recombination processes of the DSSCs based on I⁻/I₃⁻ and Co^{II}/Co^{III} redox couples, we used electrochemical impedance spectroscopy (EIS). Figure 4 shows the recombination resistance (R_{ct}) and the transport resistance (R_i) as well as the chemical capacitance (C_{μ}) for the **JK-303** cells based on the I^{-}/I_{3}^{-} and Co^{II}/ Co^{III} systems under dark conditions. The recombination resistance is higher for the Co^{II}/Co^{III} than the I^-/I_3^- redox couple in the range of applied forward bias potentials, so it is expected that the dark current would be lower for the Co^{II}/Co^{III} than the I^{-}/I_{3}^{-} system. The chemical capacitance is shifted by about 190 mV, which is due to the differences between the two redox potentials, associated with a higher recombination resistance for the Co^{II}/Co^{III} system. The density of states (DOS) between the two electrolyte systems under

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Figure 4. a) Transport resistance (R_t) , recombination resistance (R_{ct}) , and chemical capacitance (C_{μ}) of the **JK-303**-based DSSCs for I^{-}/I_{3}^{-} and $Co^{II/}$ Co^{III} under dark condition. Inset shows the charge collection efficiency of the I^{-}/I_{3}^{-} and the $Co^{II/}Co^{III}$ -based DSSCs as a function of applied bias potential. b) The electron lifetime and the transport time for I^{-}/I_{3}^{-} and $Co^{II/}Co^{III}$ as a function of forward bias potential.

dark condition, as calculated from the capacitance of the EIS,^[7b] shows a shift of about 190 mV (Figure S6 in the Supporting Information). Moreover, it is noted that the recombination resistance in both the Co^{II}/Co^{III} and the I^{-}/I_{3}^{-} systems dramatically decreases as the applied bias potential increases, because of the increase in charge carriers injected by the dye into the conduction band of TiO₂. On the other hand, the transport resistance for the Co^{II}/Co^{III} system decreased more smoothly than that of the I^-/I_3^- system. The electron lifetime ($\tau_r = C_{\mu} \times R_{ct}$) observed for the Co^{II}/Co^{III} system decreased more smoothly than that observed for the I^{-}/I_{3}^{-} electrolyte, whereas the changes in the electron transport time ($\tau_t = C_{\mu} \times R_t$) are comparable over the range of applied bias potentials.^[14] The photovoltaic performance is reflected by the charge collection efficiency (η_{cc}) derived from $\eta_{\rm cc} = (1 + R_{\rm t}/R_{\rm ct})^{-1}$ or $\eta_{\rm cc} = (1 + \tau_{\rm t}/\tau_{\rm r})^{-1}$. The $\eta_{\rm cc}$ for the Co^{II}/ Co^{III} system shows a relatively higher value at high forward bias potentials compared with that for the I^{-}/I_{3}^{-} system. The $\eta_{\rm cc}$ of the Co^{II}/Co^{III} system shows over 95% charge collection efficiency, followed by the I^-/I_3^- system with over 94% (inset in Figure 4a), although the recombination for the Co^{II}/Co^{III} system is slightly faster (Figure 4b). For the **JK-302** and **JK-304** based DSSCs using the Co^{II}/Co^{III} and the I⁻/ I_3^- systems, similar results were observed as with the **JK-303** based DSSCs (Figures S4 and S5 in the Supporting Information).

In summary, we have designed and synthesized three highly efficient organic sensitizers with sterically hindered fluorenyl units and planar indenothiophene derivatives. The photovoltaic performance is quite sensitive to structural modifications of the bridged framework. The devices based on **JK-303** using I^{-}/I_{3}^{-} , Co^{II}/Co^{III}, polymer gel, or solid state electrolytes gave conversion efficiencies of 8.69, 9.04, 7.27, and 5.82%, respectively. These efficiencies are some of the highest values reported for DSSCs based on organic sensitizers. We believe that the development of highly efficient organic sensitizers comparable to ruthenium dyes is possible through meticulous molecular engineering of dyes, and studies directed this goal are now in progress.

Experimental Section

DSSC device fabrication: Fluorine doped Tin Oxide (FTO) glass plates (Pilkington TEC Glass-TEC 8, Solar, 2.3 mm thickness) were cleaned in a detergent solution using an ultrasonic bath for 30 min and then rinsed with water and ethanol. The FTO glass plates were immersed in TiCl₄ (40 mM) at 70°C for 30 min and washed with water and ethanol. A transparent nanocrystalline layer on the FTO glass plates was prepared by screen printing TiO₂ paste (Dyesol, 18NR-T) and then drying at 120°C. The TiO₂ electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375°C for 5 min, at 450°C for 15 min, and at 500°C for 15 min. A paste for the scattering layer containing 400 nm anatase particles (CCIC, PST-400C) was deposited by screen printing and then dried for 1 h at 120 °C. The TiO₂ electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500°C for 15 min. The resulting layer was composed of a 6 µm thick transparent layer and a 3 µm thick scattering layer. The TiO₂ electrodes were treated again with TiCl₄ at 70 °C for 30 min and sintered at 500 °C for 30 min. The TiO₂ electrodes were immersed into the dye solution (0.3 mм in THF/EtOH=1:2 containing 30 mм chenodeoxycholic acid, CDCA) and kept at room temperature for 12 h. The FTO plate for the counter electrode was subsequently cleaned with an ultrasonic bath in H2O, acetone, and HCl (2 M, aq). Counter electrodes were prepared by coating with a drop of H₂PtCl₆ solution (2 mg of Pt in 1 mL of ethanol) on a FTO plate and heating at 400 °C for 15 min. The dye-adsorbed TiO₂ electrode and Pt counter electrode were assembled into a sealed sandwich-type cell by heating at 80 °C with a hot-melt film (60 µm thickness, Surlyn) as a spacer between the electrodes. A drop of electrolyte solution (iodine-based electrolyte: DMPImI (0.6 M), I2 (0.05 M), LiI (0.1 M), TBP (0.8 M) in MeCN; cobalt-based electrolyte: $[Co(bpy)_3](B(CN)_4)_2$ (0.22 M), [Co(bpy)₃](B(CN)₄)₃ (0.05 M), LiClO₄ (0.1 M), and TBP (0.8 M) in MeCN; polymer gel electrolyte: DMPImI (0.6м), I2 (0.05м), LiI (0.1м), NMBI (0.8 M), PVDF-HFP (5 wt%) in MeCN) was placed on the drilled hole in the counter electrode of the assembled cell and was driven into the cell through vacuum backfilling. Finally, the hole was sealed using additional Surlyn and a cover glass.

ssDSSCs device fabrication: The ssDSSCs were constructed by drop casting the HTM solution onto the photoelectrode and covering with a Ptcoated counter electrode, as described below. The Pt counter electrodes were prepared by drop-casting the H_2PtCl_6 solution on a FTO plate and heating at 400 °C for 15 min. The conventional compact TiO₂ layer (CC-TiO₂ film), with a 200 nm thickness, was prepared by spin coating a titanium bis(ethyl acetoacetate) solution (2 wt% in BuOH) onto FTO glass plates at 2000 rpm for 30 s, followed by calcination at 450 °C for 30 min. The commercial TiO₂ paste (solaronix D/SP) was cast onto the interfacial layer (CC-TiO2 film)-coated photoelectrode using the doctor-blade technique. The 12 μm thick nanocrystalline TiO_2 film was immersed in the dye solution (0.3 mM in THF/EtOH=1:2 containing 0.6 mM CDCA) for 4 h at room temperature. The HTM solution was prepared by dissolving 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) in ethanol. First, a few drops of dilute solution (1 wt %) were cast and dried under ambient conditions. Then, a few more drops of a more concentrated solution (3 wt% in ethanol) were directly cast onto photoelectrodes. After removing the solvent, the DBEDOT-incorporated photoelectrode was thermally polymerized at 55 °C for 24 h in an oven to produce highly conductive polymers as HTM. A drop of the acetonitrile solution containing MPII (1.0 M), TBP (0.2 M), and LiTFSI (0.2 M) was cast onto the dye-adsorbed TiO_2 electrode with conductive polymer. After evaporation of the solvent in a vacuum oven, sandwich-type ssDSSCs were fabricated through attachment of two electrodes.

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- [1] a) B. O'Regan, M. Grätzel, *Nature* 1991, 353, 737; b) M. Grätzel, *Nature* 2001, 414, 338–344.
- [2] Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, L. Y. Han, Jpn. J. Appl. Phys. 2006, 45, L638–L640.
- [3] a) M. K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, T. Bessho, M. Grätzel, *J. Am. Chem. Soc.* 2005, *127*, 16835–16847; b) Y. Cao, Y. Bai, Q. Yu, Y. Cheng, S. Liu, D. Shi, F. Gao, P. Wang, *J. Phys. Chem. C* 2009, *113*, 6290–6297; c) F. Gao, Y. Wang, D. Shi, J. Zhang, M. Wang, X. Jing, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* 2008, *130*, 10720–10728.
- [4] a) W. Zeng, Y. Cao, Y. Bai, Y. Wang, Y. Shi, M. Zhang, F. Wang, C. Pan, P. Wang, *Chem. Mater.* 2010, 22, 1915–1925; b) S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Péchy, M. Grätzel, *Chem. Commun.* 2008, 5194–5196; c) H. Choi, I. Raabe, D. Kim, F. Teocoli, C. Kim, K. Song, J.-H. Yum, J. Ko, M. K. Nazeeruddin, M. Grätzel, *Chem. Eur. J.* 2010, 16, 1193–1201.
- [5] a) S. Ko, H. Choi, M.-S. Kang, H. Hwang, H. Ji, J. Kim, J. Ko, Y. Kang, J. Mater. Chem. 2010, 20, 2391–2399; b) L.-Y. Lin, C.-H. Tsai,

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K.-T. Wong, T.-W. Huang, L. Hsieh, S.-H. Liu, H.-W. Lin, C.-C. Wu,
S.-H. Chou, S.-H. Chen, J. Org. Chem. 2010, 75, 4778–4785; c) G.
Zhang, H. Bala, Y. Cheng, D. Shi, X. Lv, Q. Yu, P. Wang, Chem. Commun. 2009, 2198–2200.

- [6] a) H. Choi, C. Baik, S. O. Kang, J. Ko, M.-S. Kang, M. K. Nazeeruddin, M. Grätzel, Angew. Chem. 2008, 120, 333–336; Angew. Chem. Int. Ed. 2008, 47, 327–330; b) K. Lim, C. Kim, J. Song, T. Yu, W. Lim, K. Song, P. Wang, N. Zu, J. Ko, J. Phys. Chem. C 2011, 115, 22640–22646; c) P. Gao, H. N. Tsao, M. Grätzel, M. K. Nazeeruddin, Org. Lett. 2012, 14, 4330–4333; d) J.-H. Chen, C.-H. Tsai, S.-A. Wang, Y.-Y. Lin, T.-W. Huang, S.-F. Chiu, C.-C. Wu, K.-T. Wong, J. Org. Chem. 2011, 76, 8977–8985.
- [7] a) S. Feldt, E. Gibson, E. Gabrielsson, L. Sun, G. Boschloo, A. Hagfeldt, J. Am. Chem. Soc. 2010, 132, 16714-16724; b) D. Zhou, Q. Yu, N. Cai, Y. Bai, Y. Wang, P. Wang, Energy Environ. Sci. 2011, 4, 2030-2034; c) Y. Bai, J. Zhang, D. Zhou, Y. Wang, M. Zhang, P. Wang, J. Am. Chem. Soc. 2011, 133, 11442-11445; d) H. N. Tsao, C. Yi, T. Moehl, J.-H. Yum, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel, ChemSusChem 2011, 4, 591-594; e) J.-H. Yum, E. Baranoff, F. Kessler, T. Moehl, S. Ahmad, T. Bessho, A. Marchioro, E. Ghadiri, J.-E. Moser, C. Yi, M. K. Nazeeruddin, M. Grätzel, Nat. Commun. 2012, 3, 631; f) M. K. Kashif, J. C. Axelson, N. W. Duffy, C. M. Forsyth, C. J. Chang, J. R. Long, L. Spiccia, U. Bach, J. Am. Chem. Soc. 2012, 134, 16646-16653.
- [8] A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W. G. Diau, C.-Y. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science* 2011, 334, 629–634.
- [9] a) C.-H. Huang, N. D. McClenaghan, A. Kuhn, J. W. Hofstraat, D. M. Bassani, Org. Lett. 2005, 7, 3409–3412; b) K. J. Hoffmann, E. Bakken, E. J. Samuelsen, P. H.-J. Carlsen, Synth. Met. 2000, 113, 39– 44.
- [10] a) V. J. Majo, P. T. Perumal, J. Org. Chem. 1996, 61, 6523; b) O. Meth-Cohn, M. Ashton, Tetrahedron Lett. 2000, 41, 2749–2752.
- [11] P. Wang, S. M. Zakeeruddin, J.-E. Moser, M. Grätzel, J. Phys. Chem. B 2003, 107, 13280–13285.
- [12] a) H. Choi, S. O. Kang, J. Ko, G. Gao, H. S. Kang, M.-S. Kang, M. D. Nazeeruddin, M. Grätzel, *Angew. Chem.* 2009, *121*, 6052–6055; *Angew. Chem. Int. Ed.* 2009, *48*, 5938–5941; b) J.-J. Kim, H. Choi, J.-W. Lee, M.-S. Kang, K. Song, S. O. Kang, J. Ko, *J. Mater. Chem.* 2008, *18*, 5223–5229.
- [13] a) J. K. Koh, J. Kim, B. Kim, J. H. Kim, E. Kim, Adv. Mater. 2011, 23, 1641–1646; b) X. Liu, W. Zhang, S. Uchida, L. Cai, B. Liu, S. Ramakrishna, Adv. Mater. 2010, 22, E150–E155; c) M. Wang, M. Xu, D. Shi, R. Li, F. Gao, G. Zhang, Z. Yi, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin, M. Grätzel, Adv. Mater. 2008, 20, 4460–4463; d) J. Burschka, A. Dualeh, F. Kessler, E. Baranoff, N. Cevey-Ha, C. Yi, M. K. Nazeeruddin, M. Grätzel, J. Am. Chem. Soc. 2011, 133, 18042–18045.
- [14] E. M. Barea, J. Ortiz, F. J. Payá, F. Fernández-Lázaro, F. Fabregat-Santiago, A. Sastre-Santos, J. Bisquert, *Energy Environ. Sci.* 2010, 3, 1985–1994.

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Molecular Engineering of Organic Sensitizers with Planar Bridging Units for Efficient Dye-Sensitized Solar Cells



Here comes the sun: Three highly efficient organic sensitizers with sterically hindered fluorenyl units and planar indenothiophene derivatives were designed and synthesized (see figure). Devices based on one of these compounds, **JK-303**, gave overall conversion efficiencies of 8.69, 9.04, 7.27, and 5.82 % using I^-/I_3^- , Co^{II}/Co^{III}, polymer gel, and solid-state electrolytes, respectively. These efficiencies are some of the highest reported for DSSCs based on organic sensitizers.