

Cyanomethylbenzoic Acid: An Acceptor for Donor- π -Acceptor Chromophores Used in Dye-Sensitized Solar Cells

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During the past two decades, dye-sensitized solar cells (DSCs) have received great attention due to their low fabrication cost compared to conventional silicon solar cells.^[1] Energy conversion efficiencies of up to 11% have been reported for DSCs based on iodide/iodine liquid electrolytes and ruthenium(II) dyes.^[2] However, in terms of practical applications, these high-performance iodine-based electrolytes are afflicted with a number of potential disadvantages, such as their high volatility, significant coloration, and corrosive nature. The latter gives rise to major incompatibility issues with a number of metals and sealing materials, limiting the use of metal substrates or charge-collecting grids in the construction of DSC modules.

Iodine-free, one-electron outer-sphere redox couples, such as cobalt(II)/(III) polypyridyl complexes, are promising alternative redox mediators due to their weak coloration and their compatibility with a wide range of metal substrates.^[3] DSCs based on these mediators can reach high conversion efficiencies, especially when used in conjunction with organic sensitizers, featuring high molar extinction coefficients and TiO₂ electrodes of only a few microns in thickness.^[4] Yella et al. recently

reported a DSC with a new benchmark efficiency of 12.3%, which used [Co(bpy)₃]^{2+/3+} (bpy = 2,2'-bipyridine) as redox mediator, causing a paradigm shift in dye-sensitized solar cells.^[5] Thus, the best-performing DSC features neither a ruthenium(II) polypyridyl complex as sensitizer, nor an iodide-based electrolyte. Previous studies suggested that the performance of cobalt redox mediators in DSCs is hindered by rapid recombination of electrons in the TiO₂ conduction band with the cobalt(III) species and, furthermore, by slow dye regeneration.^[6] These issues can be overcome by: (1) matching sensitizers with cobalt polypyridyl complexes, such that a sufficient driving force is available to ensure efficient dye regeneration,^[6] and (2) applying sensitizers with high molar extinction coefficients to ensure excellent light harvesting even when using thin TiO₂ films.^[7]

A number of organic sensitizers have been tested in conjunction with cobalt electrolytes. Most of these dyes are donor- π -bridge-acceptor (D- π -A) dyes. Among donor groups, triphenylamine and its derivatives have shown promise in the development of DSCs due to their nonplanar structure suppressing the aggregation of dye molecules.^[8] Oligothiophenes, and their derivatives, have been widely used as conjugated π -bridges, due to their high polarizability as well as their tunable spectroscopic and electrochemical properties.^[7,9] The focus of electron-acceptor groups has been largely on carboxyl acid, cyanoacrylic acid, and the rhodanine-3-acetic-acid moiety as they bind strongly to the TiO₂ semiconductor surface.^[5,10] In particular, much attention has been paid to cyanoacrylic acid because of its strong electron-withdrawing ability, which may result in an efficient electron-hole separation within the dye molecule. In contrast, few studies have ever been reported that examine whether the structural alternatives of this particular acceptor improve the performance of DSCs. In this work, cyanomethylbenzoic acid is introduced as a new acceptor moiety for DSC sensitizers and is compared to the more established cyanoacetic acid moiety. It was thought that the cyanomethylbenzoic acid may provide better performance as it will cause a redshift of the absorption spectrum. For this purpose, two new dyes were synthesized. K6 (see Figure 1) is a structural analogue of dye C240,^[11] differing slightly in the degree and type of alkoxy-substitution on the phenyl rings of the triarylamine unit. K7 is a structural analogue of K6, in which cyanoacrylic acid was replaced with the new cyanomethylbenzoic-acid acceptor. Molecular orbital calculations show similar highest occupied and lowest unoccupied molecular orbital (HOMO/LUMO) electron distributions for the two dyes (Figure 1).

The K6 and K7 dyes were synthesized by reacting the aldehyde precursor, 6-[4-(bis{4-[(2-ethylhexyl)oxy]phenyl}amino)-

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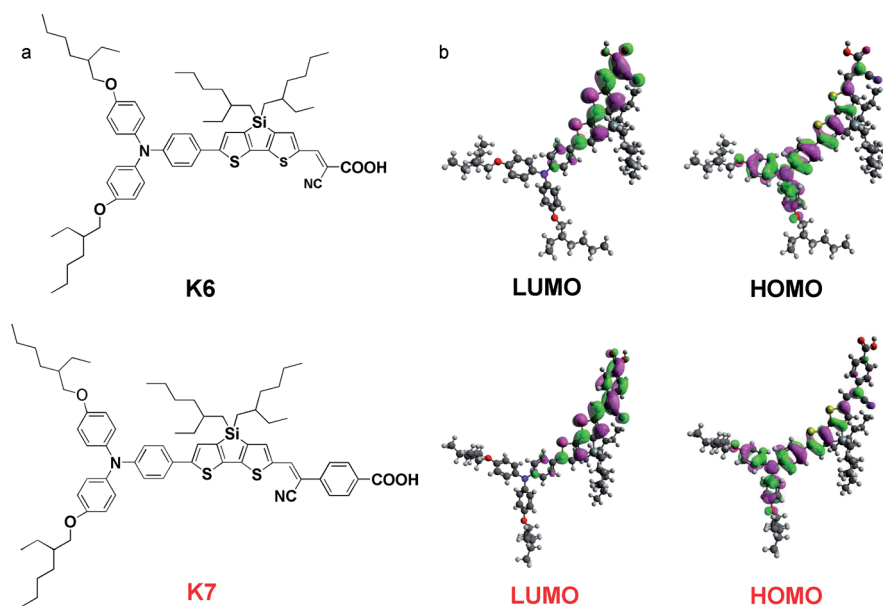


Figure 1. a) Chemical structures of sensitizers K6 and K7. b) Electron-density distribution for the LUMOs and HOMOs of K6 and K7. Density functional theory (DFT) calculations were performed on all the materials using the Gaussian 03 suite of programs and B3LYP/6-311 + G(d,p)//B3LYP/6-31G(d) level of theory.

phenyl]-4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene-2-carbaldehyde, at reflux with cyanoacetic acid in a 1:1 (v/v) acetonitrile/chloroform mixture and 4-(cyanomethyl)benzoic acid in a 9:1 (v/v) acetonitrile/chloroform solvent mixture, respectively, in the presence of piperidine as base. Synthetic and

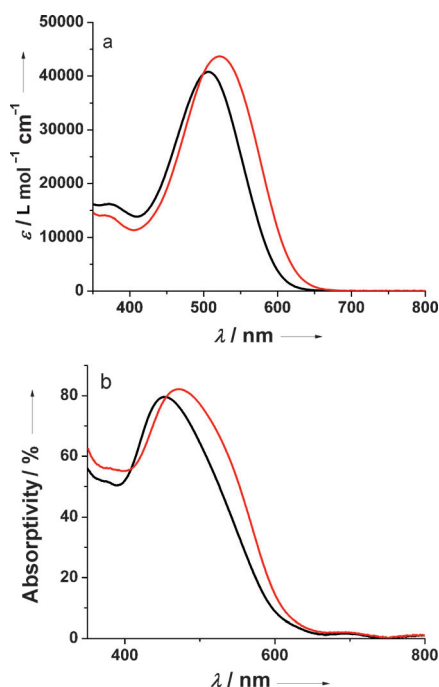


Figure 2. a) Molar extinction coefficients (ϵ) of K6 (black) and K7 (red) in chlorobenzene. b) Absorptivity spectra of 1.2 μm thick TiO_2 films sensitized with K6 (black) and K7 (red) recorded in air. Sensitization of the films was performed using a 1.5 μm dye solutions in a chlorobenzene and ethanol mixture (v/v = 1:1) for 8 h.

characterization details are provided in the Supporting Information.

The UV/Vis spectra of K6 and K7 measured in chlorobenzene solution, and when absorbed on a TiO_2 film, are shown in Figure 2. In solution, the absorption maximum of K7 is slightly red-shifted by 25 nm relative to the cyanoacrylic acid dye, K6, whereas the molar extinction coefficient at λ_{max} of K7 (43 700 $\text{L mol}^{-1} \text{cm}^{-1}$ @521 nm) is slightly higher than that of K6 (40 800 $\text{L mol}^{-1} \text{cm}^{-1}$ @506 nm). When adsorbed onto TiO_2 films, the absorption maxima for both K6 and K7 shift by about 30 nm to shorter wavelengths when compared to the solution spectrum, which may be due to the deprotonation of the carboxylic acid group on the surface of

TiO_2 . K7 shows superior light absorption at wavelengths longer than 460 nm.

The dye anchoring in DSCs is critical in achieving high cell efficiencies. K6 contains a cyanoacrylic acid group as anchoring moiety, which is typically introduced into most organic dyes to chemically attach to the TiO_2 surface.^[12] To compare the binding ability of K7, which has a cyanomethylbenzoic acid acceptor, with that of K6, the absorption of the two dyes on TiO_2 was investigated. In Figure 3, the absorption of the dye adsorbed on the mesoporous TiO_2 film is plotted as a function of the dye's equilibrium concentration (c_{equ}) in the dye bath. The two dyes show a very similar concentration-dependent absorption behavior with the dye absorption reaching a plateau at $c_{\text{equ}} \approx 0.1 \text{ mM}$. According to classical Langmuir absorption theory,^[13] the dye-binding constant can be extracted from a plot of the inverse of the surface coverage Γ^{-1} as a function of c_{equ}^{-1} [Eq. (1)].^[13] The inset of Figure 3 shows the corresponding plot, confirming Langmuir-type adsorption behavior. The calculated binding constants, K , for the two dyes are identical [(4.42 $\pm$ 0.07) $\times 10^5$ and (4.46 $\pm$ 0.03) $\times 10^5 \text{ L mol}^{-1}$ for K6 and K7, respectively], suggesting that the new acceptor moiety attaches to the TiO_2 surface just as strongly as the traditional cyanoacrylic acid group. In keeping with this finding, the dye loading for K7 [6.87 ($\pm$ 0.03) $\times 10^{-8} \text{ mol cm}^{-2}$] and K6 [6.91 ($\pm$ 0.02) $\times 10^{-8} \text{ mol cm}^{-2}$], under the conditions used to dye films for DSC construction, is identical.

$$\left(\frac{1}{\Gamma}\right) = \left(\frac{1}{c_{\text{equ}}}\right) \frac{1}{K} + 1 \quad (1)$$

Cyclic voltammetry was carried out to determine the redox properties of these two dyes (see Figure S1). The oxidation of K7 occurs at a half-wave potential of $E_{1/2}(\text{K7/K7}^+) = 1.02 \text{ V}$

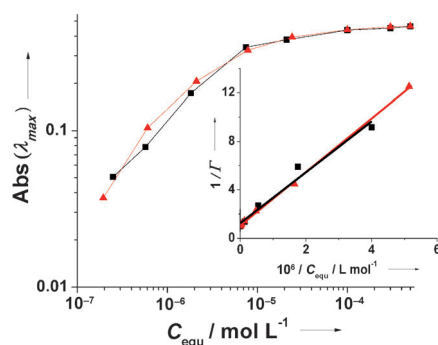


Figure 3. Langmuir isotherms. Dye absorption on 1.2 μm thick mesoporous TiO_2 films at the wavelength of maximum absorption (K6 black and K7 red) as a function of the equilibrium concentration of the dye (C_{equ}) in the solution (chlorobenzene/ethanol = 1:1 v/v). The films were kept in the dye bath for 20 h. Inset: The inverse of TiO_2 surface coverage Γ^{-1} plotted against the inverse of the dye equilibrium concentration (C_{equ}^{-1}) with $\Gamma = \text{Abs}(\lambda_{\text{max}})/\text{Abs}^0(\lambda_{\text{max}})$ where $\text{Abs}^0(\lambda_{\text{max}})$ corresponds to $\text{Abs}(\lambda_{\text{max}})$ measured at $C_{\text{equ}} = 0.5 \text{ mM}$.

versus normal hydrogen electrode (NHE). The corresponding value for K6 is 170 mV higher [$E_{1/2}(\text{K6}/\text{K6}^+) = 1.19 \text{ V}$ versus NHE]. The spectral properties of the dyes, shown in Figure 2, were combined with the electrochemical data of the dyes in solution to calculate the $E_{1/2}(\text{D}^*/\text{D}^+)$ energy levels shown in Figure 4.^[14] Based on the electrochemical properties, the dye-

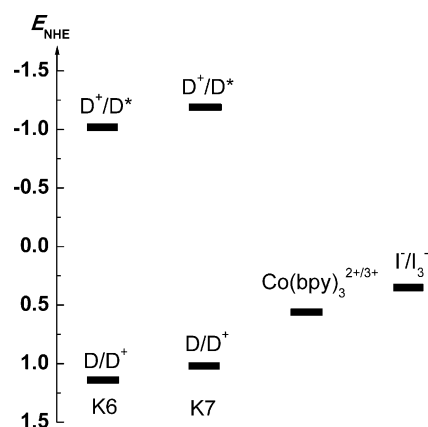


Figure 4. Energy diagram of the sensitizers K6, K7, $[\text{Co}(\text{bpy})_3]^{2+/3+}$ and a iodide/triiodide electrolyte based on the results of cyclic voltammetry measurements (see the Supporting Information).

regeneration driving forces for K6 and K7 can be estimated to be 620 and 460 mV, respectively, when these dyes are used in conjunction with a $[\text{Co}(\text{bpy})_3]^{2+/3+}$ (bpy = 2,2'-bipyridine) electrolyte. Both driving forces are in excess of 390 mV, which was previously found to be sufficient for efficient dye regeneration by the same redox mediator.^[6]

The photovoltaic performance of K6 and K7 was evaluated in DSCs constructed with $[\text{Co}(\text{bpy})_3]^{2+/3+}$ as well as a conventional triiodide/iodide-based electrolyte (see Table 1). The TiO_2 electrode structures were optimized to maximize the performance of $[\text{Co}(\text{bpy})_3]^{2+/3+}$ -based DSCs and consisted of a 4 μm thick transparent layer (30 nm particle size) and a 6 μm thick

Table 1. Photovoltaic performance of DSCs under simulated AM1.5G solar irradiation (100 mW cm^{-2}).^[a]

Dye	Electrolyte	$V_{\text{oc}}^{[b]}$ [mV]	$J_{\text{sc}}^{[c]}$ [mA cm^{-2}]	$ff^{[d]}$	$\eta^{[e]}$ [%]
K6	$\text{Co}(\text{bpy})_3^{2+/3+}$	846 ± 3	10.0 ± 0.1	0.76 ± 0.01	6.4 ± 0.2
K7		832 ± 1	12.5 ± 0.2	0.73 ± 0.01	7.6 ± 0.1
K6	I^-/I_3^-	745 ± 8	10.7 ± 0.3	0.73 ± 0.01	5.8 ± 0.2
K7		738 ± 7	11.5 ± 0.3	0.71 ± 0.01	6.1 ± 0.2

[a] DSCs were constructed with the K6 and K7 dyes and tested with two electrolyte systems the compositions of which were as follows: (1) cobalt electrolyte: 0.20 M tris(2,2'-bipyridyl)cobalt(II) bis(trifluoromethanesulfonyl)imide ($[\text{Co}(\text{bpy})_3](\text{TFSI})_2$), 0.060 M $[\text{Co}(\text{bpy})_3](\text{TFSI})_3$, 0.050 M LiTFSI, 1.00 M *tert*-butylpyridine (tBP) in acetonitrile; (2) iodide electrolyte: 0.20 M LiI, 0.060 M I_2 , 0.050 M LiTFSI, 1.00 M tBP in acetonitrile; both K6 and K7 were adsorbed from a 0.3 mM dye solution in a mixture of chlorobenzene and ethanol (v/v = 1:1) for 12 h. [b] V_{oc} is the open circuit voltage. [c] J_{sc} is the short circuit current density. [d] ff is the fill factor. [e] η is the energy conversion efficiency.

scattering layer (400 nm particle size). To facilitate the comparison of DSC performance, the concentrations of the oxidized and reduced redox mediators were chosen to be identical for both electrolyte systems. Other additives, such as tBP and LiTFSI, were also maintained at the same concentration and acetonitrile was used as solvent.

DSCs sensitized with K7 clearly outperform devices based on the K6 sensitizer in both electrolyte systems. The improvement is mostly due to an increase in the short-circuit current density (J_{sc}). The analysis of the incident-photon-to-current conversion efficiency (IPCE) measurements of these DSCs (see Figure 5a) reveals that the IPCE for K7-sensitized DSCs levels out at values of 82–86% at around 500 nm for the $[\text{Co}(\text{bpy})_3]^{2+/3+}$ - and iodide-based electrolytes, whereas the values for K6-sensitized cells are somewhat lower reaching maxima of approximately 67% for both electrolyte systems. Only the DSC based on K6 and iodide/triiodide show a weak redshift in the IPCE spectrum. The two dyes show up to 80% light absorption when adsorbed onto a 1.2 μm thick TiO_2 film (see Figure 2b). Light harvesting by the sensitized TiO_2 layers used for the construction of these DSCs (4 μm thick + scattering layer) will, therefore, be close to quantitative over a significant range of the spectral region around the absorption maxima of the sensitizers. To further rationalize the observed IPCE spectra of K6 and K7 in $[\text{Co}(\text{bpy})_3]^{2+/3+}$ -based DSCs, absorbed-photon-to-electron (APCE) spectra were calculated based on the absorption properties of the sensitized films (see Figure 5b). The average APCE values across the spectral range of 450–550 nm for K6 and K7 are 63 and 70%, respectively, indicating a significantly increased charge conversion efficiency per adsorbed photon for K7-sensitized $[\text{Co}(\text{bpy})_3]^{2+/3+}$ -based DSCs. This increase can be caused by: (1) improved charge injection; (2) improved dye-regeneration; and/or (3) reduced recombination. To check whether the observed photocurrents during the IPCE and APCE measurements were limited by charge collection, preliminary front/back-IPCE measurements were performed (Figure S3 in the Supporting Information). The results show negligible charge recombination during electron diffusion through TiO_2

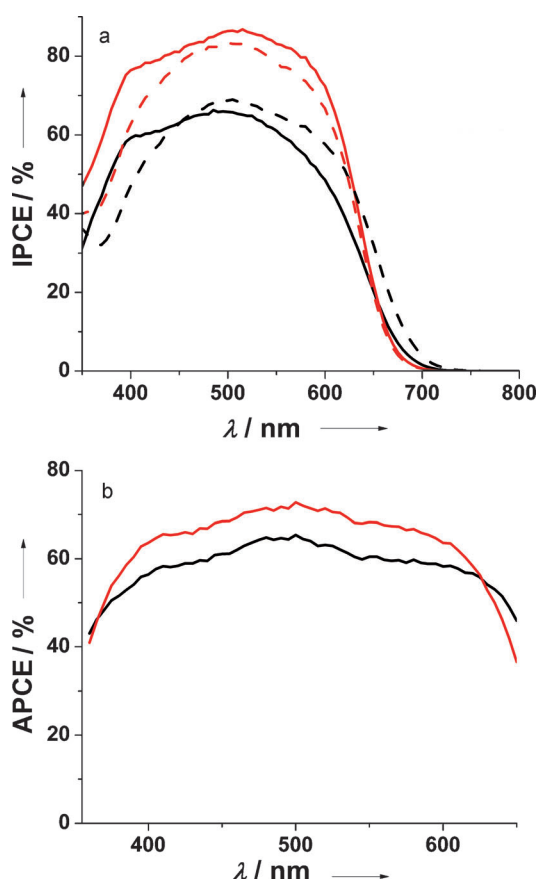


Figure 5. a) Incident-photon-to-electron conversion efficiencies (IPCEs) of DSCs sensitized with K6 (black) and K7 (red) based on $[\text{Co}(\text{bpy})_3]^{2+/3+}$ (solid line) and I^-/I_3^- (dashed line) electrolytes (same devices as reported in Table 1). b) Absorbed-photon-to-current generation efficiencies (APCEs) as a function of wavelength for K6 (black) and K7 (red) in conjunction with the $[\text{Co}(\text{bpy})_3]^{2+/3+}$ electrolyte described in Table 1. DSCs based on 4 μm thick transparent TiO_2 films were used for this analysis.

film, suggesting that the electron diffusion length is well below the thickness of the TiO_2 film.

To further elucidate the origin of the observed differences in photovoltaic performance, the electron lifetime and mean transit time of photo-injected charge carriers were studied by means of intensity modulated photovoltage and photocurrent spectroscopy (IMVS and IMPS)^[15] in combination with charge extraction experiments. The IMPS results, shown in Figure 6a, indicate that similar mean electron transit times were observed for both dyes and both electrolytes and suggest comparable electron transport within the TiO_2 layer in all cases. Charge extraction measurements according to Duffy et al.^[16] were used to determine the amount of charge stored in DSCs as a function of V_{OC} (see Figure S3). The results obtained through IMVS and charge extraction experiments were then combined to yield the electron lifetime as a function of charge stored in the DSC, as shown in Figure 6b. The results for the $[\text{Co}(\text{bpy})_3]^{2+/3+}$ electrolytes clearly show an increase in electron lifetime by about a factor of 1.6 for K6-sensitized DSCs over devices sensitized with K7. When I^-/I_3^- is used as redox mediator, there is no apparent difference in electron lifetime for K6- and K7-sen-

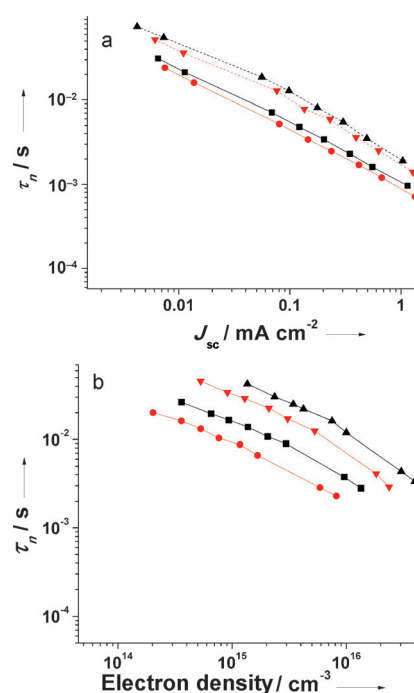


Figure 6. IMVS and IMPS measurements performed on K6- (black) and K7- (red) sensitized DSCs based on $[\text{Co}(\text{bpy})_3]^{2+/3+}$ (solid line) and I^-/I_3^- (dashed line) electrolytes (same devices as reported in Table 1). a) Mean charge transient time versus short circuit current. b) Electron lifetime versus electron density.

sitized DSCs. The somewhat longer electron lifetime observed for K6-sensitized devices is also consistent with the 14 mV increase in V_{OC} and slightly higher ff for K6, relative to K7-sensitized $[\text{Co}(\text{bpy})_3]^{2+/3+}$ DSCs (see Table 1). This rules out both increased charge recombination as well as inefficient dye-regeneration as a cause for the inferior performance of K6-sensitized DSCs as both effects should result in a reduction, rather than an increase, in electron lifetime. Consequently, superior charge injection properties for K7, relative to K6, are the most likely origin of the observed performance difference. This is also consistent with a 170 mV more negative $E_{1/2}(\text{K7}^+/\text{K7}^*)$ level compared to $E_{1/2}(\text{K6}^+/\text{K6}^*)$ (see Figure 4).

In summary, we have evaluated a new cyanomethylbenzoic acid as acceptor for D- π -A DSC sensitizers by comparing its performance to the more widely used cyanoacrylic acid acceptor unit in a pair of analogous dyes. These dyes were modeled on previously reported sensitizers that yielded high DSC performances when combined with $[\text{Co}(\text{bpy})_3]^{2+/3+}$ electrolytes (C240).^[11] The dye featuring the cyanomethylbenzoic acid acceptor (K7) outperformed the model sensitizer comprising the cyanoacrylic acid group (K6) in terms of its photovoltaic performance. Superior charge injection properties of K7 compared to K6 were identified as the most likely reasons for the observed increases in J_{sc} , efficiency; and IPCE. The performance increase could be realized in spite of a slight electron lifetime decrease for $[\text{Co}(\text{bpy})_3]^{2+/3+}$ -based DSCs when the cyanoacrylic acid group is replaced with cyanomethylbenzoic acid.

Progress in the development of alternative redox mediators and metal-free sensitizers has accelerated significantly in recent years. The recent work by Yella et al.^[5] has highlighted the potential for efficiency improvements beyond those of classical DSCs based on iodide and ruthenium(II) polypyridyl complexes. Until now, however, a limited number of organic dyes have been reported to act as efficient sensitizers when used in conjunction with cobalt(II)/(III) polypyridyl redox mediators. This is anticipated to change radically, given the remarkable progress accomplished recently.^[3,4,17] New sensitizers will be required with properties tailored towards their use in conjunction with alternative non-corrosive electrolytes. We believe that the cyanomethylbenzoic-acid acceptor reported herein represents a valuable addition to the library of acceptors that will form the basis for the next generation of custom-designed high-efficiency sensitizers.

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