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Enhanced Acceptor Character in Fullerene Derivatives. Synthesis and Electrochemical Properties of Fulleropyrrolidinium Salts

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Abstract: A family of *N*-methylpyrrolidinium fullerene iodide salts, possessing one (or two) solubilizing chain(s), has been synthesized. As evidenced by CV and steady-state voltammetry experiments, carried out in tetrahydrofuran (THF) solutions, these species show enhanced electron-accepting properties with respect to both the parent fulleropyrrolidines and C_{60}. CV measurements performed at −60 °C and scan rates of 50 V/s, made possible by the use of ultramicroelectrodes, have allowed the observation, for the first time in fullerene derivatives, of six fullerene-centered reductions. Bulk electrolysis of these novel compounds, performed at the stage of the first reduction potential, generates a stable zwitterion, with both anion and cation located on the fullerene derivative.

Introduction

The modification of the electronic properties of C_{60} is a major goal in the synthetic organic chemistry of fullerenes.[1−4] C_{60} is an excellent acceptor, as shown in cyclic voltammetry experiments, where six reversible one-electron reduction waves can be seen;[5−7] in alkali-metal intercalated complexes, which show superconductivity;[8,9] and in charge-transfer salts, which exhibit ferromagnetic properties.[10] Furthermore, and very interestingly, C_{60} is a great partner for light-induced electron-transfer processes, holding strong promise in the fabrication of photovoltaic devices.[3,11,12] During the evolution of the fullerene chemistry, it seemed feasible to modulate the electronic properties of the derivatives, as happens with other classes of materials, for instance, with quinones.[13] However, most of C_{60} derivatives have decreased electronegativity,[14,15] and attempts to increase the electron affinity of C_{60} have led only to partial success.[16−18] Major effort in this direction has been spent by the Wudl laboratory, with the attachment of strong electron-withdrawing groups[19,20] or through the periconjugation mechanism[21,22] and the heterofullerene synthesis.[23] A dependence of photoluminescence from the accepting ability inside a collection of Wudl compounds has also been reported.[24] It is clear that the improvement of the electron-accepting properties of C_{60}, coupled with the versatility of the organic chemistry of fullerenes, may lead to new and, hopefully, more efficient behavior in charge-transfer processes. In this paper we report the synthesis and electrochemical properties of a series of pyrrolidinium salt derivatives of C_{60}, which show enhanced electron-accepting properties with respect to both the parent pyrrolidine derivatives and C_{60}. Moreover, CV measurements performed at low temperatures and fast scan rates, using ultramicroelectrodes, have allowed the observation, for the first time in fullerene derivatives, of six C_{60}-centered reductions.

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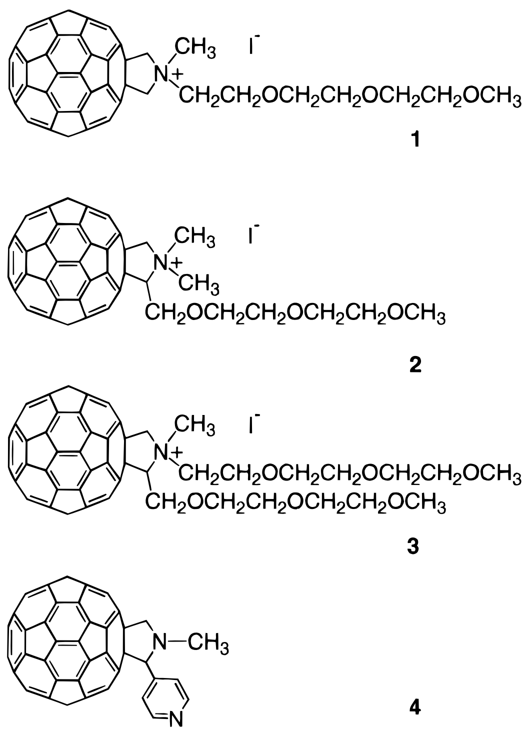
Scheme 1



Results and Discussion

Compounds **1**−**3** (Scheme 1) were prepared by methylation of the corresponding pyrrolidines[25−27] in excess methyl iodide.[28−30] The reactions were performed in chloroform at 80 °C in closed vials. The ammonium salts precipitated, and the solids were washed several times with toluene. Compound **3** was an analytically pure mixture of two diastereoisomers. Salts **1**−**3** are moderately soluble in tetrahydrofuran, methylene chloride, dimethyl sulfoxide, and dimethyl sulfoxide−water.

The CV curve for a 0.2 mM **1** THF solution at 0.1 V/s and 25 °C is shown in Figure 1a.

Six reduction peaks are observed, labeled by increasing Roman numbers. In the anodic region, an irreversible one-electron oxidation peak is observed, with $E_p = 0.62$ V (0.2 V/s, 25 °C) which corresponds to the irreversible oxidation of iodide counterion. The first four peaks in Figure 1a show an anodic counterpart in the reverse scan and include one-electron reversible redox couples, whose $E_{1/2}$ are reported in Table 1.

The chemical and electrochemical reversibility of these redox couples was checked in CV curves in which the potential was reversed after each peak. Peaks V and VI lack their corresponding anodic partners, which is also missing when the potential is reversed immediately after peak V, indicating the instability of the five-electron-reduced species. Peak VI follows the chemically irreversible process V and cannot be safely attributed to a sixth reduction of **1**.

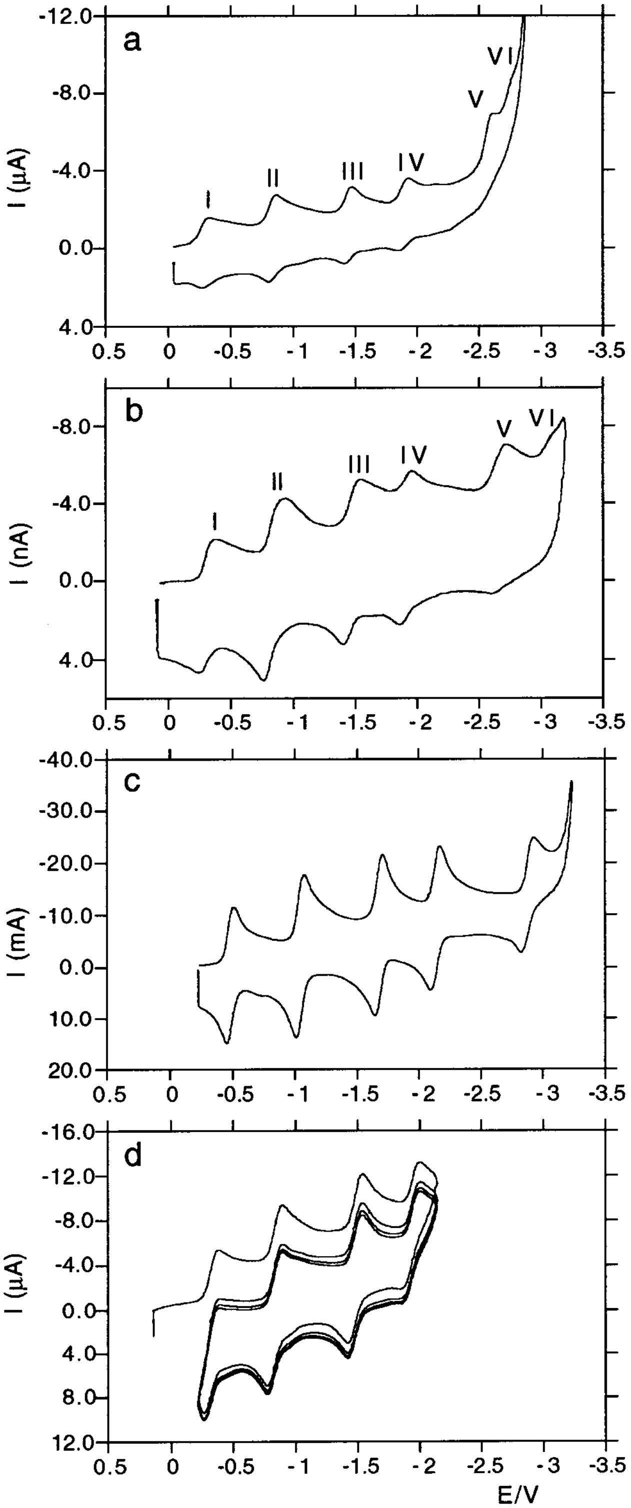


Figure 1. CV curves for a 0.2 mM **1**, 0.05 M $^{n}Bu_4NPF_6$ (TBAH), THF solution: (a) $v = 0.5$ V/s; $T = 25$ °C, working electrode, Pt wire (0.15 cm^2); (b) $T = -75$ °C, $v = 50$ V/s; working electrode, Pt disk UME (10 μm diameter). (c) CV curve for a 0.2 mM **4**, 0.05 M TBAH, THF solution: $v = 0.5$ V/s; $T = -60$ °C; working electrode, Pt wire (0.15 cm^2). (d) CV curves for a 0.2 mM **1**, 0.05 M TBAH, THF solution: $T = -75$ °C; $v = 1$ V/s; working electrode, Pt wire (0.15 cm^2).

The CV behavior of **2** and **3** is not significantly different from that of **1** except for small shifts of $E_{1/2}$ values for the corresponding processes and minor morphological changes likely associated to slightly different solubilities (Table 1).

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Table 1. $E_{1/2}$ or E_p Values (V vs SCE) for Compounds **1**−**5** and C_{60} (Measurements at 25 °C were taken under conditions of Figure 1a. At −60 °C, data were taken according to Figure 1b for compounds **1**−**3** or according to Figure 1c for compounds **4**, **5**, and C_{60})

compd	*T* (°C)	I	II	III	IV	V	VI
1	25	−0.29	−0.79	−1.34	−1.84	-2.64^a	-2.79^a
	−60	−0.31	−0.84	−1.47	−1.90	−2.66	-3.15^b
2	25	−0.29	−0.81	−1.34	−1.85	-2.66^a	-2.77^a
	−60	−0.32	−0.85	−1.49	−1.92	−2.68	-3.15^b
3	25	−0.29	−0.79	−1.36	−1.85	-2.63^a	-2.80^a
	−60	−0.33	−0.86	−1.50	−1.92	−2.68	-3.15^b
4	25	−0.47	−1.06	−1.68	−2.15	−2.86	
	−60	−0.49	−1.06	−1.68	−2.13	−2.87	
5[c]	25	−0.30	−0.80	−1.43	−1.80		
	−60	−0.37	−0.89	−1.51	−1.97	-2.76^a	-3.06^a
$\mathbf{C_{60}}$	25	−0.35	−0.94	−1.50	−1.99	−2.50	
	−60	−0.38	−0.95	−1.53	−2.02	−2.55	−3.01

[a] Irreversible, E_{pc} measured at 0.5 V/s. [b] Irreversible, $E_{1/2}$ estimated by digital simulation. [c] Oxidation of the ferrocene unit detected at +0.69 V (25 °C) or +0.63 V (−60 °C).

The effect of increasing scan rate and/or lowering temperature on the CV morphology was then investigated. The relatively low solubility of **1**−**3** in THF and the very high resistivity of THF−TBAH solutions restrict greatly the scan rate/temperature range in which useful information can be obtained by traditional CV technique. In this respect, ultramicroelectrodes offer better opportunities: despite the unfavorable faradaic/capacitive current ratios, wider scan rate (up to several hundreds V/s) and temperature (down to −75 °C) ranges are allowed with respect to macroelectrodes. As the scan rate was increased and temperature lowered, the height of peak V gradually decreased and, at the same time, an anodic counterpart of peak V developed, eventually corresponding to a reversible redox couple with $E_{1/2} = -2.66$ V (at −60 °C), Figure 1b. It should be noted that peak VI is still observed, and although its anodic partner is missing, its height is comparable to that of the previous peaks, indicating that peak VI may represent the sixth reduction step of **1**. As a matter of fact, the morphology of the CV curves in Figure 1b documents the complexity of the voltammetric behavior of **1**, under the present conditions, which results in large $E_{pc} - E_{pa}$ separations, uneven peak heights, and unusual triangularly shaped peaks. This is particularly evident when comparing these curves to that, obtained under the same conditions, for the representative fulleropyrrolidine derivative **4** (Scheme 1), shown in Figure 1c. In this case, five one-electron reversible processes are observed. No sixth peak is observed close to the almost vertical base solution discharge. While the larger $E_{pc} - E_{pa}$ separations as well as the lower faradaic/capacitive current ratios in the curve of Figure 1b with respect to that of Figure 1c are not unexpected, the other morphological characteristics in the curve of Figure 1b suggest adsorption phenomena associated to the redox processes. Figure 1d shows the repetitive-scan CV curve obtained under the conditions of Figures 1b but at a rate of 1 V/s. The scan is limited in this case to the first four redox steps (under these conditions the fifth peak is irreversible), and as expected for the much lower scan rate, a better-shaped curve is obtained with respect to the previous ones.

Particularly remarkable is the observation of six fullerene-centered reduction processes for **1**−**3**. Five processes at most, cf. Figure 1c, have been reported for fulleropyrrolidine and methanofullerene derivatives.[3] The possible observation of a sixth reduction of fullerene moiety in some fulleroids was suggested,[31] but such a hypothesis was not uncontroversial for the complications associated to either fulleroid−methanofullerene isomerization or a ring-opening mechanism operating in the multiply reduced species.[32] The present study would therefore represent the first case in which the sixth fullerene-centered reduction is assessed in a fullerene derivative.

Among possible applications, electron-acceptors better than C_{60} are of interest in the elaboration of supramolecular machineries in which the photoinduced intramolecular charge-transfer represents an important act. Owing to the exponential dependence of the intramolecular charge-transfer rate constant, k_{cs}, on driving force, $DG°_{cs}$,[33] the anodic shift by a few hundred millivolts for the first reduction of the fullerene derivatives, playing the role of the electron acceptor when coupled to a suitable donor, may mean the increase of k_{cs} by several order of magnitude.[33] However, the stability of the reduced acceptor is also of fundamental importance since its chemical degradation would also severely reduce the lifetime of the CS species. As a matter of fact, nearly all the compounds showing better acceptor character than C_{60} exhibit irreversible behavior even under CV time scale.[16,17,19−22]

The stability of the reduced forms of **1**−**3**, already assessed on the CV time scale, was therefore checked on a much longer time scale by performing spectroelectrochemical experiments. A 0.2 mM **1**, 0.05 M TBAH benzonitrile solution was electrolyzed at −0.5 V. This corresponds to the first reduction of the species ($E_{1/2}{}^{I} = -0.38$V in benzonitrile). As the electrolysis proceeded, the typical absorption features in the visible and NIR regions of fullerene-centered monoanion appeared and developed in the spectra: the NIR absorption maximum occurred at 1027 nm, somewhat between the corresponding absorptions for C_{60} (1075 nm) and **4** (998 nm) radical anions respectively measured under similar conditions. The electrolyzed solution remained stable for several hours. It should be noted that we are dealing with a zwitterion: the negative charge, situated on the C_{60} spheroid, is balanced by the positive charge of the covalently linked ammonium salt.

In conclusion, a new class of fullerene derivatives which show enhanced electron-acceptor character is reported. The reason for the increased electronegativity is, so far, to be attributed to simple inductive effects. Theoretical computations are currently underway for a deeper insight. The occurrence of the reduction peaks at less negative potentials in cyclic voltammetry coupled with use of ultramicroelectrodes has allowed the detection of a sixth reduction step in a C_{60} derivative. Since the chemistry of fulleropyrrolidines is very rich,[34] a large use of the methodology reported in the present manuscript can be envisaged, especially in donor−bridge−acceptor dyads containing fulleropyrrolidinium ions. As a preliminary example, we have prepared compound **5**, via azomethine ylide cycloaddition to C_{60},[35] followed by methylation (Scheme 2).

Compound **5** retains the acceptor character typical of pyrrolidinium salts, as easily seen from CV experiments (Table 1). The ferrocene unit, covalently attached, should act as efficient electron/energy donor in photoinduced processes.[36] Photophysical studies on this system are in progress.

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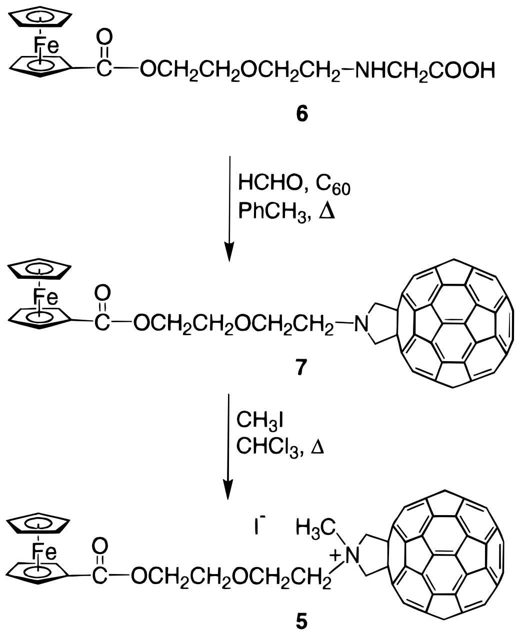
Scheme 2



Experimental Section

Instrumentation. Details regarding instrumentation and methods used to characterize the compounds considered in this paper have been described elsewhere.[37]

Materials. C_{60} was purchased from Bucky USA (99.5%). Fulleropyrrolidine precursors to compounds **1**−**3** were prepared according to published procedures.[25−27] N-Substituted glycine **6** was synthesized as described elsewhere.[38]

General Procedure for the Synthesis of Fulleropyrrolidinium Salts 1−3. A chloroform solution (2 mL) containing 48 μmol of fullerene derivative and 0.3 mL (100 equiv) of methyl iodide was heated for 3 days at 80 °C in a closed (screw-cap) vial. The solvent was evaporated to dryness; the solid residue was transferred into a centrifuge tube, washed several times with toluene, and dried under vacuum. Yields are usually quantitative (TLC), but the amounts of material recovered after the washings depend on the relative solubility of the salts in toluene.

Iodide salt **1**: yield 98%. ^{1}H NMR (200 MHz, DMSO-d_6): δ 5.80 (s, 2H), 4.53 (m, 2H), 4.30 (m, 2H), 4.20 (s, 2H), 3.80 (m, 2H), 3.68 (m, 2H), 3.57 (m, 2H), 3.42 (m, 2H), 3.35 (s, 3H), 3.20 (s, 3H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 152.6, 151.8, 146.9, 145.9, 145.7, 145.6, 145.2, 145.1, 144.9, 144.8, 144.0, 142.7, 142.3, 141.7, 141.6, 141.5, 141.1, 141.0, 139.4, 139.3, 136.1, 135.9, 72.5, 71.3, 69.7, 69.5, 68.5, 64.7, 64.4, 58.2, 58.0, 48.7, 48.5. IR (KBr): ν (cm^{-1}) 2985, 2881, 2816, 1433, 1111. UV−vis (CH_2Cl_2): λ_{max} nm 253, 316, 429, 463, 543. APCI-MS (THF−methanol 4:1): *m*/*z* 924 (M$^+$). Anal. Calcd for $C_{70}H_{22}INO_3$ (1051.865): C, 79.93; H, 2.11; N, 1.33. Found: C, 77.9; H, 2.09; N, 1.35.

Iodide salt **2**: yield 68%. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 6.50 (dd, J = 3.3 and 9.4 Hz, 1H), 6.28 (d, J = 12.6 Hz, 1H), 5.89 (d, J = 12.6 Hz, 1H), 5.03 (dd, J = 3.3 Hz, J = 12.4 Hz, 1H), 4.82 (dd, J = 9.4 and 12.4 Hz, 1H), 4.44 (s, 3H), 4.33 (s, 3H), 4.01 (m, 1H), 3.89 (m, 1H), 3.78 (m, 2H), 3.69 (m, 2H), 3.56 (m, 2H), 3.39 (s, 3H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 152.4, 151.3, 150.9, 149.4, 146.9, 145.9, 145.6, 145.4, 145.2, 145.1, 145.0, 144.7, 144.1, 144.0, 143.9, 142.8, 142.7, 142.4, 142.3, 141.7, 141.7, 141.5, 141.4, 141.1, 141.0, 140.9, 140.7, 139.7, 139.4, 139.2, 139.1, 136.8, 136.1, 136.0, 135.4, 78.5, 74.0, 71.3, 71.1, 70.1, 69.5, 67.5, 66.5, 58.2, 54.9, 46.2. IR (KBr): ν (cm^{-1}) 2945, 2877, 2813, 2193, 1719, 1466, 1112. UV−Vis (CH_2Cl_2): λ_{max} nm 253, 316, 428, 475. APCI-MS (THF−methanol 4:1): *m*/*z* 924 (M$^+$).

Iodide salt **3**: yield 50%. ^{1}H NMR (200 MHz, CD_2Cl_2) = two diastereoisomers in 70/30 ratio: major isomer, δ 6.66 (dd, J = 3.0 and 9.4 Hz, 1H), 6.44 (d, J = 12.5 Hz, 1H), 5.74 (d, J = 12.5 Hz, 1H), 5.24 (m, 1H), 5.05 (m, 1H), 4.86 (m, 2H), 4.32 (s, 3H), 4.01−3.49 (m, 16H), 3.27 (s, H), 3.37 (s, 3H); minor isomer, diagnostic peaks, δ 6.24 (d, J = 13.1 Hz, 1H), 6.09 (s, 1H), 5.88 (d, J = 12.5 Hz, 1H), 4.43 (s, 3H), 3.39 (s, 3H), 3.30 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 152.0, 151.9, 150.0, 149.3, 149.1, 148.9, 147.5, 147.4, 146.5, 146.3, 146.0, 145.8, 145.6, 145.5, 145.2, 144.9, 144.8, 144.7, 144.6, 144.5, 144.5, 144.3, 144.3, 143.2, 143.2, 142.8, 142.3, 142.2, 142.0, 141.9, 141.8, 141.1, 141.0, 140.9, 140.6, 140.2, 140.1, 140.0, 136.6, 136.3, 135.8, 73.2, 71.9, 71.8, 71.2, 71.1, 71.0, 70.8, 70.4, 70.3, 70.2, 68.3, 67.9, 67.4, 66.2, 59.1, 45.6. IR (KBr): ν (cm^{-1}) 2973, 2875, 2817, 1463, 1104. UV−vis (CH_2Cl_2): λ_{max} nm 253, 314, 376, 428. APCI-MS (THF−methanol 4:1): *m*/*z* 1057 (M$^+$).

Synthesis of Ferrocene-Containing Fulleropyrrolidinium Salt 5. A toluene solution of C_{60} (300 mg, 0.41 mmol), glycine derivative **6**[38] (231 mg, 0.615 mmol), and paraformaldehyde (61.5 mg, 2.05 mmol) was refluxed for 40 min. The solvent was evaporated, and the crude was purified by flash column chromatography to obtain 43 mg (10%) of compound **7**: ^{1}H NMR (200 MHz, $CDCl_3/CS_2$): δ 4.83 (broad s, 2H), 4.52 (broad s, 4H), 4.31 (s, 2H), 4.22 (s, 5H), 4.08−3.91 (m, 4H), 3.45 (m, 2H). ^{13}C NMR (200 MHz, C_6D_6/CS_2): δ 170.7, 155.4, 147.6, 146.6, 146.4, 146.0, 145.6, 144.9, 143.5, 143.0, 142.6, 142.4, 142.2, 140.5, 136.7, 77.6, 71.7, 71.0, 70.8, 70.6, 70.3, 69.8, 68.8, 63.3, 54.5, 54.4. IR (KBr): ν (cm^{-1}) 2953, 2921, 2852, 1699, 1455, 1375, 1274, 1124, 767, 735. UV−vis (CH_2Cl_2): λ_{max} nm 238, 262, 324, 436, 696. APCI-MS (THF−methanol 4:1): *m*/*z* 1063 (M$^+$).

Iodide salt **5** was prepared according to the the general procedure (see above). Yield: 35%. ^{1}H NMR (200 MHz, DMSO-d_6): δ 5.78, (AB system, 4H), 4.72 (s, 2H), 4.58−4.32 (m, 6H), 4.39 (s, 2H), 4.21 (s, 8H), 3.95 (m, 2H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 175.6, 157.5, 156.6, 151.8, 150.9, 150.6, 150.6, 150.2, 150.1, 150.0, 149.8, 149.7, 149.0, 148.9, 147.7, 147.6, 147.3, 147.2, 146.6, 146.5, 146.4, 146.0, 145.9, 144.4, 144.3, 141.0, 140.7, 133.9, 133.1, 130.3, 77.5, 76.4, 75.5, 74.8, 74.6, 73.8, 73.5, 69.9, 69.4, 68.0, 53.4. IR (KBr): ν (cm^{-1}) 2953, 2922, 2852, 1699, 1457, 1273, 1125, 767, 733. UV−vis (CH_2Cl_2): λ_{max} nm 238, 264, 324, 436, 700. APCI-MS (THF−methanol 4:1): *m*/*z* 1078 (M$^+$).

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