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Tetrahedron Letters 47 (2006) 8323–8327
Tetrahedron Letters

First syntheses and electronic properties of (oligo)phenothiazine–C_{60} dyads

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Received 1 August 2006; revised 11 September 2006; accepted 18 September 2006
Available online 9 October 2006

Abstract—(Oligo)phenothiazine–C_{60} dyads **3** can be readily synthesized by a three-component condensation–cycloaddition of the corresponding (oligo)phenothiazinyl carbaldehydes **1**, *N*-hexyl glycine (**2**), and C_{60}. Cyclic voltammetry of **3** and reference compounds **4** shows that the phenothiazinyl moiety (donor) and the fullerene fragment (acceptor) are electronically decoupled in ground state. However, upon UV excitation the phenothiazinyl fluorescence is considerably quenched, presumably as a consequence of a charge separation by an intramolecular photo-induced electron transfer from phenothiazine to fullerene.

The design of well-defined photoactive molecular electron donor (D) and electron acceptor (A) systems, that is, D–A dyads,[1] is an ongoing research field and a fundamental basis for the development of molecular electronic devices (photoswitches, nonlinear optical materials, photoconductive molecular wires),[2] artificial photosynthetic systems,[1] and with the prospect of nanodimensioning[3,4] the ultimate goal is the construction of light driven molecular motors and machines.[5] In the past years besides porphyrine-acceptor dyads and triads,[6] especially, covalently linked fullerenes have been applied as almost ideal acceptor moieties as a consequence of several favorable electronic properties and similarities to C_{60}.[6,7] Furthermore, excited states and the C_{60}-radical anion derivatives display distinct absorption bands in the near IR allowing reliable assignments of transient species in time-resolved absorption spectroscopy. As donor components there have been employed metal and free-base porphyrines with manifold nonconjugating bridging geometries, *para*-phenylene diamines, polycondensed aromatic hydrocarbons, transition metal complexes, carotenoids, ferrocenes, phthalocyanines, and quite recently, also strong donors such as tetrathiafulvalenes (TTF), thienylenevinylenes, and oligothiophenes, with charge separations upon PET (photoinduced electron transfer) close to unity.[2,8] Covalent linkage of donors to fullerenes to furnish fullerene-donor dyads is accomplished in three different modes: by [1+2]-cyclopropanation by Bingel, by [3+2]-pyrrolidine formation, and by Diels–Alder cycloaddition.[6,7,9] Among numerous organic and organometallic donor molecules phenothiazine and its derivatives, due to their reversible oxidation,[10,11] have become attractive electrophores in PET systems with transition metal coordination compounds as photoexcitable acceptor moieties,[12] also in conjunction with oligonucleotides as bridging units,[13] in charge transfer compounds, either as CT-complexes[14] or conjugatively linked D–A-systems.[15] Although the intermolecular PET of C_{60} and phenothiazines has been studied in the past[16] neither the syntheses nor the intramolecular PET of covalently bound phenothiazine–C_{60} dyads have been investigated so far and remain challenging goals. In continuation of our program to synthesize and study alkylated[17] and arylated bi- and terphenothiazines,[18] we have recently reported on acceptor substituted phenothiazines and their intramolecular charge-transfer properties.[19] Here, we communicate the first synthesis and electronic properties of (oligo)PT–C_{60} (PT = *N*-hexyl phenothiazine) dyads that can be suitable for intramolecular PET.

Prato's three-component condensation of an aldehyde, an *N*-alkyl glycine and C_{60} in the presence of a 1,3-dipolar cycloaddition of in situ formed azomethine ylides to fullerene represents a direct and versatile strategy to donor-C_{60}-dyads.[7g,20] Therefore, upon reacting (oligo)PT aldehyde derivatives **1**, *N*-hexyl glycine **2**, and C_{60} in boiling toluene for 16–20 h the $(PT)_n$–$(C_6H_4)_m$–C_{60}-dyads **3** can be isolated after chromatography on

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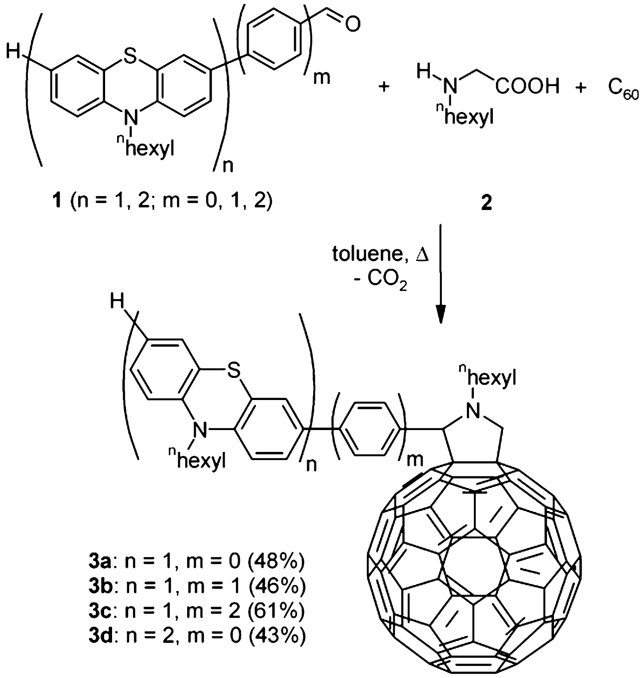
0040-4039/$ - see front matter
doi:10.1016/j.tetlet.2006.09.076



Scheme 1. Three-component cyclocondensation of (phenothiazine)$_n$-(C_6H_4)$_m$–C_{60} dyads **3**.

silica gel in 43–61% yield (Scheme 1) as black–brown amorphous solids.[21]

The structures of these novel phenothiazine–C_{60} dyads **3** are unambiguously supported by ^{1}H and ^{13}C NMR spectra, IR spectroscopy, MALDI-TOF mass spectrometry and HRMS. The electronic ground state of these non conjugated D–A dyads is best characterized by cyclic voltammetry. Hence, in the cyclic voltammograms of the phenothiazine–C_{60} dyads **3** the distinct appearance of the three reversible waves in the cathodic region can be attributed to the first three C_{60} centered reduction events (Table 1, Fig. 1). Comparison to C_{60} and pyrrolidine–C_{60} reveals that the reductions are shifted cathodically by 100–150 mV upon phenothiazinyl substitution. The reversible waves in the anodic region are phenothiazine centered oxidations, which appear for mono PT derivatives **3a–c** and for the diPT derivative **3d** at the expected potential as the model compounds **5–8** within experimental error. The HOMO–LUMO gaps of the dyads **3** can be directly calculated from $E_0^{0/+1}$ and $E_0^{0/-1}$.

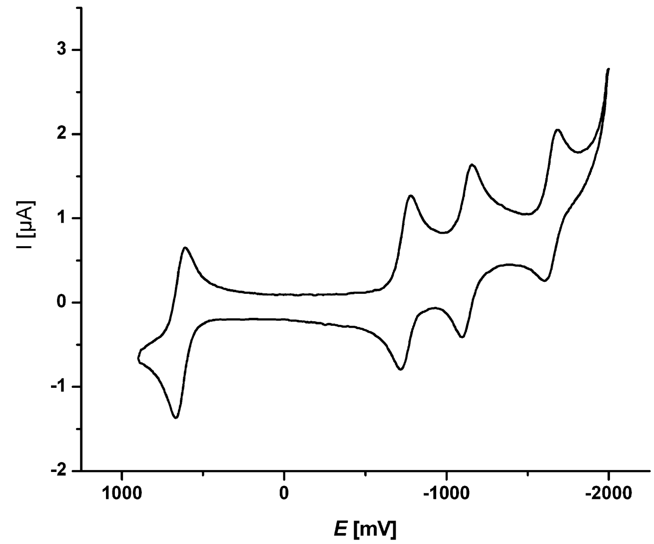


Figure 1. Cyclic voltammogram of PT–C_6H_4–C_{60} (**3b**). Recorded in dichloromethane at 20 °C, 0.1 M N^{n}Bu$_4$PF$_6$ (CH_2Cl_2), Pt as working electrode, Ag/AgCl as reference electrode, and Pt as counter electrode.

In comparison to the model compounds **4–8**, the UV/vis spectra of dyads **3** are clearly dominated by the appearance of the phenothiazine absorptions, whereas the pyrrolidine–C_{60} absorptions (**4**) can only occasionally be identified. Therefore, the minimal influence of the C_{60}–pyrrolidine annulation can be interpreted that in the ground state the phenothiazine donors and the C_{60} acceptor are expectedly electronically decoupled. This

Table 1. Selected redox potentials and UV/vis data of phenothiazine and C_{60} derivates, and phenothiazine–C_{60} dyads **3** (PT = *N*-hexyl phenothiazine, *N*-hexyl phenothiazin-3-yl, or *N*-hexyl phenothiazin-3,7-diyl) (recorded in dichloromethane at 20 °C, 0.1 M N^{n}Bu$_4$PF$_6$, Pt as working electrode, Ag/AgCl as reference electrode, and Pt as counter electrode)

	$E_0^{0/+1}$ (mV)	$E_0^{0/-1}$ (mV)	$E_0^{-1/-2}$ (mV)	$E_0^{-2/-3}$ (mV)	$\Delta E_{HOMO-LUMO}$ (mV)	λ_{max} (ε) (nm)
PT–pyrrolidine–C_{60} (**3a**)	735	−678	−1059	−1581	1413	246 (52,300), 258 (67,200), 312 (15,400), 322 (15,400)
PT–C_6H_4–pyrrolidine–C_{60} (**3b**)	698	−683	−1059	−1578	1381	256 (38,300), 266 (252,000), 324 (93,100)
PT–(C_6H_4)$_2$–pyrrolidine–C_{60} (**3c**)	696	−689	−1068	−1575	1385	246 (96,800), 258 (108,900), 270 (98,000), 298 (60,300), 306 (57,300), 322 (49,000), 392 (11,300)
(PT)$_2$–pyrrolidine–C_{60} (**3d**)	646					
	801	−681	−1061	−1585	1327	248 (117,500), 258 (133,700), 268 (499,000), 324 (4400)
C_{60}	—	−560	−950	−1410	—	—
pyrrolidine–C_{60} (**4**)	—	−567	−964	−1414	—	258 (220,200), 330 (67,800), 378 (14,100)
PT (**5**)	728	—	—	—	—	258 (30,900), 312 (4900)
PT–C_6H_5 (**6**)	701	—	—	—	—	236 (20,100), 268 (35,200), 320 (8500)
PT–C_6H_4–C_6H_5 (**7**)	700	—	—	—	—	270 (50,400), 292 (21,900), 328 (14,800)
PT– PT (**8**)	642					
	788	—	—	—	—	268 (47,800), 282 (40,000), 322 (18,600), 350 (14,300), 360 (13,600)
PT–pyrrolidine–C_{60} (**3a**)	735	−678	−1059	−1581	1413	246 (52,300), 258 (67,200), 312 (15,400), 322 (15,400)

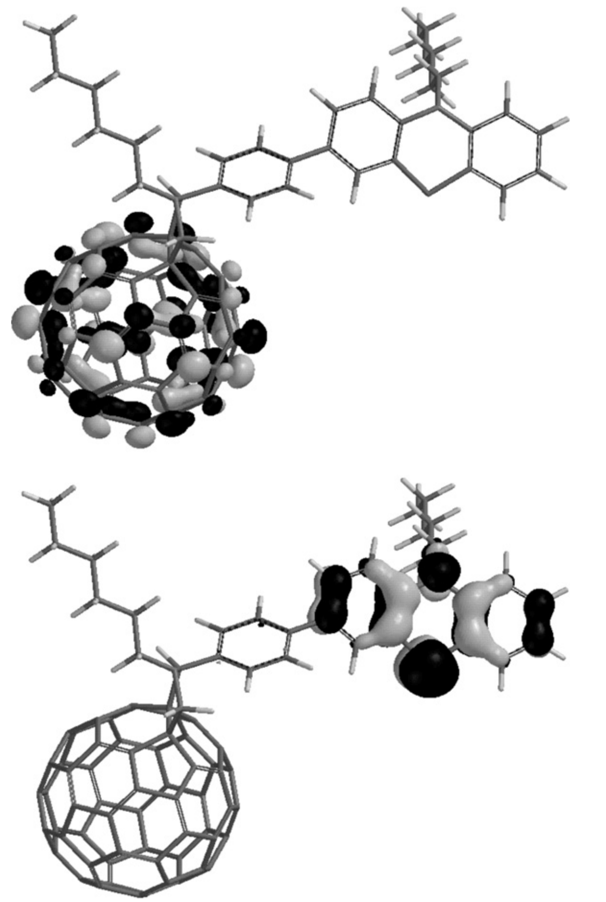


Figure 2. HOMO (bottom) and LUMO (top) of dyad **3b** (PM3 calculation).

view is additionally supported by the calculated electronic structure of the frontier molecular orbitals of dyads **3b** and **3d** (Fig. 2). Semiempirical calculations on the PM3 level of theory[22] clearly show that the HOMOs are localized in the (oligo)phenothiazine moiety, whereas the LUMOs are exclusively fullerene centered.

However, upon photonic excitation a significant interaction of the (oligo)phenothiazine and the fullerene units can be detected by fluorescence spectroscopy. In comparison to the model compounds **5–8** a considerable quenching of the phenothiazine located fluorescence of dyads **3** can be detected upon recording the static fluorescence (Fig. 3). With the exception of *N*-hexyl phenothiazine (**5**), the other (oligo)phenothiazine models **6–8** fluorescence with significant intensity and can be applied as suitable probes. Therefore, at comparable concentrations (10^{-5} M) in dyads **3** the emission intensity from the (oligo)phenothiazine part is efficiently quenched. The range of quenching is 3.5 times (**3a**), 4.5×10^3 times (**3b**), 5×10^2 times (**3c**), and 4.5×10^9 times (**3d**) with respect to the model compounds **5–8**. Simultaneously, no energy transfer from phenothiazine to C_{60} can be detected by fluorescence spectroscopy. Taking into account all electronic parameters of dyads **3**, apparently, the rapid and efficient depopulation of the S_1 excited state by PET from (oligo)PT to C_{60} can be conceived.

In conclusion, we have disclosed a straightforward access to (oligo)PT–C_{60} dyads by applying Prato's three-component synthesis. These novel donor-fullerene dyads are expectedly electronically decoupled in the electronic ground state as shown by UV/vis spectroscopy, cyclic voltammetry and semiempirical calculation. Yet, this ground state decoupling is favorable for an efficient and rapid depopulation of the excited singlet state of the (oligo)phenothiazine moiety as supported by measurements of the static fluorescence of both dyads and (oligo)phenothiazine models. Therefore, a PET process seems to be most likely. Further investigations will address the photophysics of these and related dyads by time-resolved laser spectroscopy. Syntheses and characterizations of suitable systems are currently in progress.

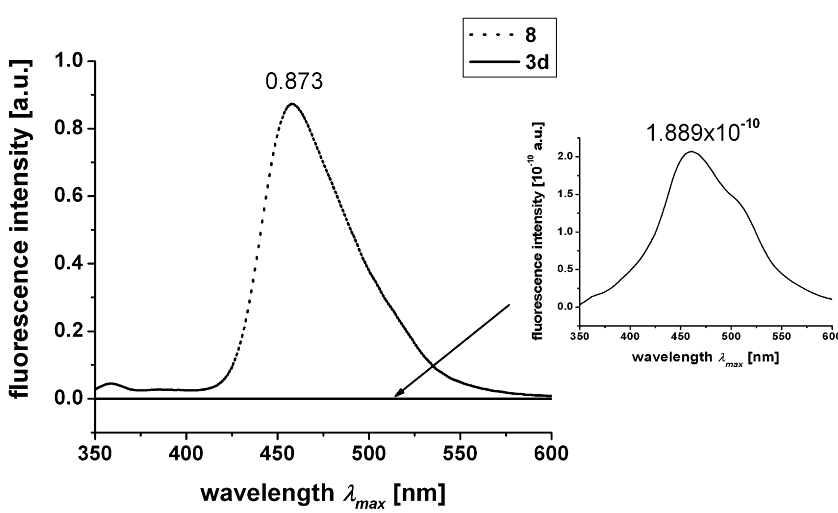


Figure 3. Normalized fluorescence spectra of **8** (dotted line) and **3d** (solid line) (recorded in CH_2Cl_2 at 20 °C, inset: amplified residual fluorescence of **3d**).

Acknowledgments

The financial support of the Volkswagenstiftung and the Fonds der Chemischen Industrie is gratefully acknowledged. We also cordially thank the BASF AG for the generous donation of chemicals.

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21. Typical procedure (dyad **3b**): In a 1 L three-necked round bottom flask, 346 mg (0.48 mmol) of C_{60} and 318 mg (2.00 mmol) of N-^{n}hexyl glycine (**2**) were dissolved under heating to reflux in 400 mL of toluene to give a magenta solution. Then, 155 mg (0.40 mmol) of aldehyde **1b** ($n = m = 1$) in 100 mL of toluene was added dropwise to the solution and heating at reflux temperature was continued for 18 h. After cooling to room temp and removal of the solvent, the residue was purified by chromatography on silica gel (n-hexane, cyclohexane,

cyclohexane/dichloromethane) to give 219 mg (46%) of **3b** as an amorphous black brown powder, Mp. 203 °C. ^{1}H NMR (300 MHz, CS_2/CD_2Cl_2 5:1): δ 0.95 (t, $J = 6.9$ Hz, 3H), 1.04 (t, $J = 6.9$ Hz, 3H), 1.31–2.08 (m, 16H), 2.58–2.68 (m, 1H), 3.26–3.35 (m, 1H), 3.88 (t, $J = 7.1$ Hz, 2H), 4.18 (d, $J = 9.3$ Hz, 1H), 5.11 (s, 1H), 5.16 (d, $J = 9.3$ Hz, 1H), 6.82 (dd, $J = 1.0$, 8.1 Hz, 1H), 6.86–6.92 (m, 2H), 7.06 (dd, $J = 1.6$, 7.6 Hz, 1H), 7.13 (ddd, $J = 1.6$, 7.3, 8.1 Hz, 1H), 7.31 (d, $J = 2.1$ Hz, 1H), 7.36 (dd, $J = 2.1$, 8.4 Hz, 1H), 7.58 (d, $J = 8.5$ Hz, 1H), 7.84 (br, 2H). ^{13}C NMR (75 MHz, CS_2/CD_2Cl_2 5:1): δ 15.1 (CH_3), 15.3 (CH_3), 23.9 (CH_2), 24.0 (CH_2), 27.7 (CH_2), 27.8 (CH_2), 28.1 (CH_2), 28.3 (CH_2), 29.5 (CH_2), 32.6 (CH_2), 33.0 (CH_2), 48.3 (CH_2), 67.6 (CH_2), 69.5 (C_{quat}), 77.3 (C_{quat}), 83.1 (CH), 115.9 (CH), 116.0 (CH), 123.2 (CH), 125.2 (C_{quat}), 126.2 (C_{quat}), 126.3 (CH), 126.4 (CH), 127.2 (2 CH), 127.9 (CH), 128.0 (CH), 130.6 (2 CH), 135.2, 136.4, 136.5, 136.6, 137.2, 137.5, 140.2, 140.58, 140.62, 140.82, 140.84, 142.2, 142.3, 142.47, 142.55, 142.62, 142.64, 142.71, 142.72, 142.75, 142.77, 142.90, 142.92, 143.16, 143.18, 143.2, 143.3, 143.6, 143.71, 143.76, 145.00, 145.03, 145.27, 145.28, 145.3, 145.7, 145.81, 145.85, 145.86, 145.9, 146.0, 146.07, 146.1, 146.16, 146.2, 146.4, 146.52, 146.53, 146.68, 146.7, 146.77, 146.8, 146.85, 146.9, 146.93, 147.1, 147.4, 147.85, 147.9, 154.0, 154.1, 154.8, 157.1 (C_{quat}). FAB/HR MS calcd. for $^{13}C^{12}C_{91}H_{41}N_2S$: 1206.3024; found: 1206.3093; Calcd. for $^{12}C_{92}H_{41}N_2S$: 1205.2990; found: 1205.3062 [M+H^{+}]. Calcd. for $^{13}C^{12}C_{91}H_{40}N_2S$: 1205.2946; found: 1205.3062; Calcd. for $^{12}C_{92}H_{40}N_2S$: 1204.2912; found: 1204.2932 [M^{+}]. Anal. calcd. for $C_{92}H_{40}N_2S$ (1205.4): C, 91.67; H, 3.34; N, 2.32; S, 2.66. Found: C, 91.49; H, 3.62; N, 2.24; S, 2.65.

22. Applying the PM3 method as implemented in *PC Spartan Pro*, Wavefunction Inc.: Irvine, CA, **1999**.