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Synthesis and electronic properties of (oligo)phenothiazine-ethynyl-hydro-C_{60} dyads

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Abstract—Ethynyl bridged (oligo)phenothiazine–C_{60} dyads **2** can be readily synthesized by addition of the corresponding (oligo)phenothiazinyl lithium acetylides **1** to C_{60} followed by protonation with acetic acid. Cyclovoltammetric data of **1** and **2** reveal that the (oligo)phenothiazinyl moieties (donor) and the fullerene fragment (acceptor) are electronically decoupled in ground state, yet, each additional phenothiazine lowers the HOMO–LUMO gap by 100 mV. 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.

Donor–acceptor dyads[1] are key functional units in molecular electronic devices (photoswitches, nonlinear optical materials, and photoconductive molecular wires),[2] and artificial photosynthetic systems.[1] Very often porphyrines adopt the donor role in dyads and triads[3] and covalently linked fullerenes have been identified to be the almost ideal acceptor moieties as a consequence of several favorable electronic properties and similarities to C_{60}.[3–5] In addition, distinct absorption bands in the near IR of excited states and C_{60}-radical anion derivatives allow reliable assignments of transient species by time-resolved absorption spectroscopy. Besides porphyrines donors like *para*-phenylene diamines, polycondensed aromatic hydrocarbons, transition metal complexes, carotenoids, ferrocenes, phthalocyanines, and quite recently, also strong donors such as tetrathiafulvalenes (TTF), thienylene–vinylenes, and oligothiophenes display charge separations upon PET (photo-induced electron transfer) close to unity.[2,6] Furthermore, phenothiazine and its derivatives, due to their reversible oxidation,[7,8] have become attractive electrophores in PET systems with transition metal coordination compounds as photoexcitable acceptor moieties,[9] also in conjunction with oligonucleotides as bridging units,[10] in charge transfer compounds, either as CT-complexes[11] or conjugatively linked D–A-systems.[12] Although the intermolecular PET of C_{60} and phenothiazines has been studied in the past,[13] syntheses and electronic properties of covalently bound phenothiazine–C_{60} dyads have remained unexplored so far. In this context, the quenching of the fluorescence in phenothiazine moieties can serve as a suitable probe for intramolecular PET. In recent years, we have established fluorescent alkynylated (oligo)phenothiazines,[14] arylated bi- and terphenothiazines,[15] and quite recently, we have reported on acceptor substituted phenothiazines and their intramolecular charge-transfer properties.[16] Here, we communicate the synthesis and electronic behavior of ethynyl bridged (oligo)phenothiazine–C_{60} dyads with tunable PET properties.

Alkynylated phenothiazines are blue to green fluorescent electroactive chromophores with absorptions below 400 nm. They can be readily synthesized with fine-tunable electronic properties.[14] Komatsu has introduced a straightforward access to alkynyl substituted fullerene derivatives by smoothly adding lithium acetylides to C_{60}.[17] Therefore, upon deprotonating alkynylated (oligo)phenothiazines **1** with ^{n}BuLi at 0 °C and adding C_{60} to the reaction mixture the resulting anion is quenched with acetic acid to give rise to the formation of (oligo)phenothiazinyl-ethynyl-hydro-C_{60} derivatives **2** in moderate yields as black-brown amorphous solids (Scheme 1).[18] The structures of these novel (oligo)phenothiazine–C_{60} dyads **2** are unambiguously supported by ^{1}H and ^{13}C NMR spectra, IR spectroscopy, MALDI-TOF mass spectrometry, and HRMS.

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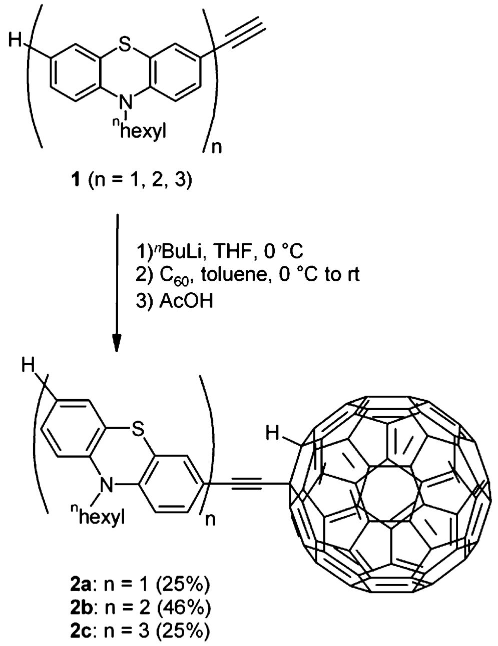

Scheme 1. Synthesis of (phenothiazine)$_n$–C≡C–C$_{60}$ dyads **2**.

Cyclic voltammetry is an appropriate tool to study the nature of the electronic ground state of these non conjugated D–A dyads. Hence, in the cyclic voltammograms of the phenothiazine–C$_{60}$ dyads **2** 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$_{60}$ reveals that the reductions are almost not affected by phenothiazinyl ethynyl substitution. The reversible waves in the anodic region are (oligo)phenothiazine centered oxidations which appear at the same potentials as the model compounds **1** within experimental error. The HOMO–LUMO gaps of the dyads **2** can be directly calculated from $E_0^{0/+1}$ and $E_0^{0/-1}$.

Interestingly, the cyclic voltammograms of dyads **2** can be interpreted as a superposition of the individual donor and acceptor component, indicating their mutual electronic decoupling in the electronic ground state. Since the first oxidation is lowered by 100 mV with each phenothiazine unit that is introduced, simultaneously the HOMO–LUMO gap lowers in a linear fashion. In comparison with the model compounds **1**, the UV/vis spectra of dyads **2** are clearly dominated by the appearance of the phenothiazine absorptions. The longest wave length maxima are identical and display a large extinction coefficient. As no charge transfer bands can be identified, in the ground state the (oligo)phenothiazine donors and the C$_{60}$ acceptor are expectedly electronically decoupled. This view is additionally supported by the calculated electronic structure of the frontier molecular orbitals of dyad **2b** (Fig. 2). Semiempirical calculations on the PM3 level of theory[19] clearly show that the HOMO and HOMO-1 are localized in the diphenothiazine moiety, whereas the LUMO is exclusively fullerene centered.

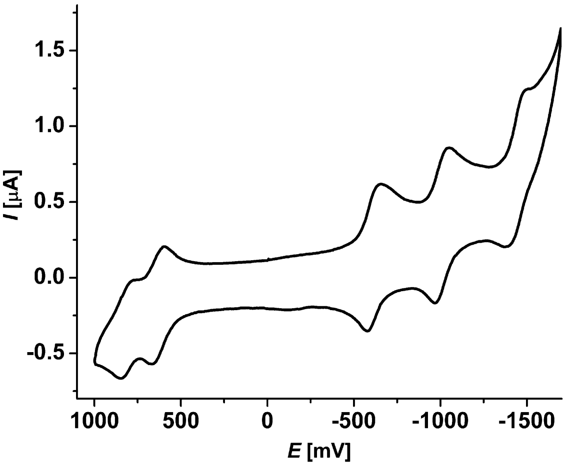

Figure 1. Cyclic voltammogram of (phenothiazine)$_2$–C≡C–C$_{60}$H (**2b**). Recorded in dichloromethane at 20 °C, 0.1 M N^{n}Bu$_4$PF$_6$ (CH$_2$Cl$_2$), Pt as working electrode, Ag/AgCl as reference electrode, and Pt as counter electrode.

However, upon photonic excitation a significant interaction of the (oligo)phenothiazine and the fullerene units can be detected by fluorescence spectroscopy. In comparison with the model compounds **1**, dyads **2** are nonfluorescent as detected upon recording the static fluorescence (Fig. 3).

At comparable concentrations (10^{-6} M) in dyads **2**, the emission intensity from the (oligo)phenothiazine part is efficiently quenched. The range of quenching is 1.0×10^3 times (**2a**), 0.7×10^3 times (**2b**), and 4.0×10^3 times (**2c**) with respect to the model compounds **1**. Simultaneously, no energy transfer from phenothiazine to C$_{60}$ can be de-

Table 1. Selected redox potentials and UV/vis data of phenothiazine derivatives **1**, C$_{60}$, and (phenothiazine)$_n$–C≡C–C$_{60}$ dyads **2**

	$E_0^{0/+1}$ (mV)	$E_0^{+1/+2}$ (mV)	$E_0^{+2/+3}$ (mV)	$E_0^{0/-1}$ (mV)	$E_0^{-1/-2}$ (mV)	$E_0^{-2/-3}$ (mV)	$\Delta E_{\text{HOMO–LUMO}}$ (mV)	$\lambda_{\max}$ (ε) (nm)
PT–C≡C–C$_{60}$H (**2a**)	791	—	—	−564	−957	−1398	1355	258 (201,100), 330 (68,500)
(PT)$_2$–C≡C–C$_{60}$H (**2b**)	664	841	—	−586	−979	−1413	1250	258 (170,400), 330 (55,500)
(PT)$_3$–C≡C–C$_{60}$H (**2c**)	611	758	881	−547	−941	−1389	1158	258 (226,500), 280 (110,800), 330 (747,00)
C$_{60}$	—	—	—	−560	−950	−1410	—	—
PT–C≡C–H (**1a**)	801	—	—	—	—	—	—	268 (37,700), 324 (7000)
(PT)$_2$–C≡C–H (**1b**)	663	842	—	—	—	—	—	264 (46,600), 278 (58,800), 328 (19,000), 370 (15,400)
(PT)$_3$–C≡C–H (**1c**)	608	762	872	—	—	—	—	280 (74,500), 330 (258,000), 360 (23,800)

(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).

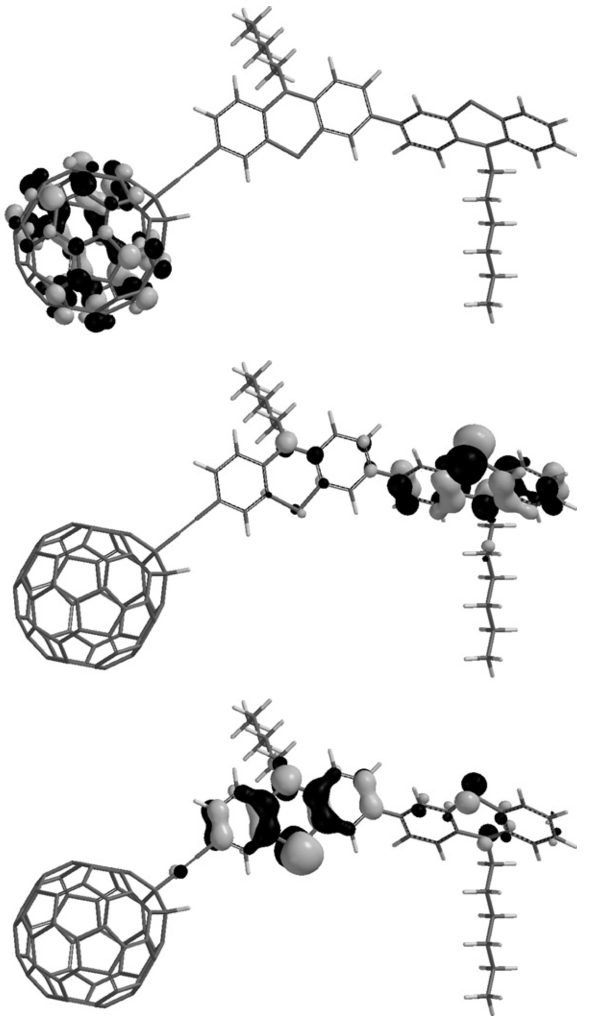

Figure 2. HOMO-1 (bottom), HOMO (middle), and LUMO (top) of dyad **2b** (PM3 calculation).

tected by fluorescence spectroscopy. With respect to all electronic parameters of dyads **2**, 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 ethynyl bridged (oligo)phenothiazine–C_{60} dyads by applying Komatsu's fullerene alkynylation. The resulting donor–fullerene dyads represent superpositions of their constituting components and are expectedly electronically decoupled in the electronic ground state as shown by UV/vis spectroscopy, cyclic voltammetry, and semiempirical calculation. Yet, the ground state decoupling is responsible for an efficient, 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. Obviously, the extent of the intramolecular PET is rather independent on the number of phenothiazine units. Further investigations will address the photophysics of PT–fullerene dyads by time-resolved laser spectroscopy. Syntheses and characterizations of suitable systems are currently in progress.

Acknowledgements

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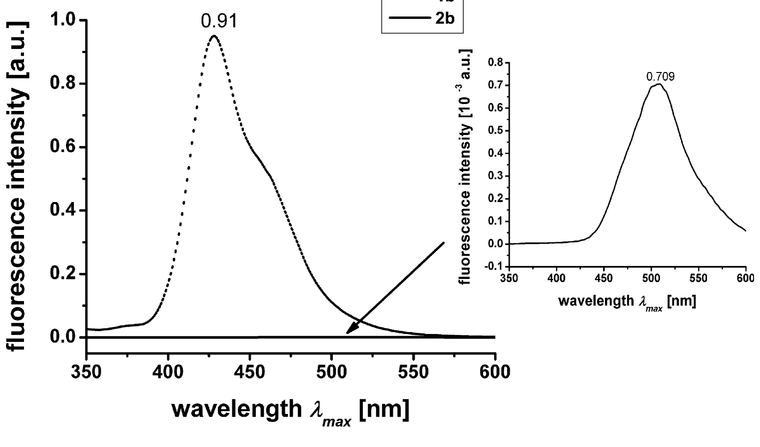

Figure 3. Normalized fluorescence spectra of **1b** (dotted line) and **2b** (solid line) (recorded in CH_2Cl_2 at 20 °C, inset: amplified residual fluorescence of **2b**).

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18. Typical procedure (dyad **2b**): In a degassed Schlenk flask, 348 mg (0.44 mmol) of C_{60} was dissolved and stirred for 40 min at room temperature in 70 mL of anhydrous toluene to give a magenta solution. In another Schlenk flask, a solution of 235 mg (400 μmol) of alkyne **1b** in 3 mL of anhydrous, degassed THF was deprotonated at 0 °C with 250 μL (398 μmol) of 1.59 M ^{n}BuLi in hexanes and stirring at that temperature was continued for 20 min. Then, acetylide solution was added dropwise to the C_{60} solution at 0 °C and stirring was continued at room temperature for 40 min. Then, 0.1 mL of acetic acid was added to the reaction mixture. The solvents were removed in vacuo and the darkbrown residue was purified by chromatography on silica gel (*n*-hexane, cyclohexane, cyclohexane/dichloromethane) to give 219 mg (46%) of **1b** as a black brown solid, mp >350 °C. ^{1}H NMR (300 MHz, CS_2/CD_2Cl_2 5:1):δ 0.91–1.01 (m, 6H), 1.31–1.45 (m, 12H), 1.79–1.95 (m, 4H), 3.89 (t, $J = 6.9$ Hz, 2H), 3.95 (t, $J = 6.9$ Hz, 2H), 6.84 (d, $J = 8.3$ Hz, 1H), 6.87 (d, $J = 8.3$ Hz, 1H), 6.88–6.92 (m, 2H), 7.08 (dd, $J = 1.5$, 7.8 Hz, 1H), 7.12–7.15 (m, 3H), 7.25 (dd, $J = 2.2$, 10.4 Hz, 1H), 7.28–7.32 (m, 1H), 7.49 (d, $J = 1.9$ Hz, 1H), 7.56 (dd, $J = 1.9$, 8.3 Hz, 1H). ^{13}C NMR (75 MHz, CS_2/CD_2Cl_2 5:1): δ 15.05 (CH_3), 15.08 (CH_3), 23.86 (CH_2), 23.89 (CH_2), 27.68 (CH_2), 27.69 (CH_2), 27.76 (CH_2), 27.79 (CH_2), 32.55 (CH_2), 32.56 (CH_2), 48.27 (CH_2), 48.49 (CH_2), 55.87 ($C_{\text{quat.}}$), 62.66 (CH), 84.22 ($C_{\text{quat.}}$), 93.02 ($C_{\text{quat.}}$), 115.59 (CH), 115.87 (CH), 116.06 (CH), 116.33 (CH), 116.95 ($C_{\text{quat.}}$), 123.17 (CH), 125.18 ($C_{\text{quat.}}$), 125.31 ($C_{\text{quat.}}$), 125.48 ($C_{\text{quat.}}$), 125.77 (CH), 125.82 (CH), 126.02 (CH), 127.86 (CH), 127.90 (CH), 128.03 (CH), 131.47 (CH), 132.04 (CH), 134.55, 135.35, 135.54, 136.78, 140.97, 141.04, 142.27, 142.36, 142.57, 142.66, 142.7, 142.78, 143.21, 143.24, 143.85, 144.12, 144.71, 145.17, 145.34, 145.37, 145.98, 146.06, 146.14, 146.24, 146.30, 146.32, 146.44, 146.84, 146.85, 147.02, 147.03, 147.32, 147.98, 148.22, 152.02, 152.19 ($C_{\text{quat.}}$). FAB/HR MS calcd for $^{13}C^{12}C_{97}H_{41}N_2S_2$: 1310.2745. Found: 1310.2689. Calcd for $^{12}C_{98}H_{41}N_2S_2$: 1309.2711. Found: 1309.2670 [$M+H^+$]. Calcd for $^{13}C^{12}C_{97}H_{40}N_2S_2$: 1309.2667. Found: 1309.2670. Calcd for $^{12}C_{98}H_{40}N_2S_2$: 1308.2633. Found: 1308.2607 [M^+]. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 2951 (w), 2923 (w), 2851 (w), 1604 (w), 1459 (m), 1334 (w), 1248 (w), 1183 (w), 874 (w), 806 (w), 746 (w), 578 (w), 527 (m). UV/vis (CH_2Cl_2): λ_{max} (ε) 258 nm (170,400), 330 (55,500). Anal. Calcd for $C_{98}H_{40}N_2S_2$ (1309.6): C, 89.88; H, 3.08; N, 2.14; S, 4.90. Found: C, 89.88; H, 2.93; N, 1.84; S, 4.54.
19. Applying the PM3 method as implemented in *PC Spartan Pro*, Wavefunction Inc.: Irvine, CA, 1999.