Phenothiazine-Aromatic Hydrocarbon Acceptor Dyads as Photo-induced Electron Transfer Systems by Ugi Four-Component Reaction

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A phenothiazynyl donor moiety can be covalently coupled to aromatic hydrocarbon acceptor units via Ugi four-component reaction in an efficient, rapid, and highly convergent fashion. These novel phenothiazine-acceptor dyads are electronically decoupled in the electronic ground state according to UV/Vis spectroscopy and cyclic voltammetry. In the excited state the inherent acceptor luminescence is substantially quenched. Calculations of the Gibbs energy of photo-induced electron transfer from readily available UV/Vis spectroscopic and cyclovoltammetric data according to the Weller approximation rationalizes the feasibility of the reductive electron transfer from phenothiazine to the aromatic hydrocarbon upon photoexcitation.

Key words: Absorption Spectroscopy, Cyclic Voltammetry, Chromophores, Fluorescence, Multicomponent Reactions, Photo-induced Electron Transfer

Introduction

Chromophores, fluorophores and electrophores constitute as functional organic materials [1] the active components in molecular electronics [2], photonics [3], and bioanalytics [4–6]. Among them, molecules with electron donor (Do) and acceptor (Acc) substitution, i.e. Do-Acc dyads, have received considerable interest [7, 8]. Most dominantly, Do-Acc systems have found application in molecular electronics and optoelectronics [9–14], organic light-emitting diodes (OLEDs) [15–19], and photovoltaic devices [20–24]. While the persistent light-induced charge separation between a donor and an acceptor is exemplified in photosynthesis for converting sunlight into chemical energy, the generation of electrical energy from sunlight has become a lead for identifying artificial photovoltaic systems [25, 26]. On this basis various types of Do-Acc dyads have been intensively studied [27, 28]. Besides photo-induced electron transfer (PET) [29–33] with donors such as porphyrines, polycyclic aromatic hydrocarbons, perylenediimides, and (oligo)thiophenes [34, 35], also phenothiazine and its derivatives [36–39] have become attractive electrophores as a consequence of reversible and tunable oxidation potentials. In addition the quenching of the phenothiazine-inherent fluorescence offers a facile evidence for the occurrence of intramolecular PET in phenothiazine containing Do-Acc dyads [40, 41]. Besides C60 fullerene derivatives [42–44], 9,10-anthraquinones have been commonly employed in Do-Acc arrangements [45–50]. For instance, phenothiazine-anthraquinone couples have been attached to peptide scaffolds [51–53], and they have also been incorporated in rigidified Do-Acc dyads [54].

In recent years the concept of diversity-oriented syntheses of chromophores [55–62] was established to access chromophores in a one-pot fashion based upon transition metal-catalyzed consecutive multicomponent [63–65] and domino processes [66]. We also reasoned that the Ugi four-component reaction (Ugi 4CR) [67–70], generating the chemically robust α-aminoacyl amide backbone in one step and with high diversity, promises a straightforward access to phenothiazine-anthraquinone dyads (Fig. 1) [71]. In addition we could identify a photo-induced electron transfer leading to a charge-separated state with a life-
time of > 2 ns, as elucidated by femtosecond transient absorption spectroscopy.

Encouraged by this study we also became interested in annelated aromatic hydrocarbons as acceptor moieties, which can serve as fluorescence quenching probes for a quick, semiquantitative estimation of the accessibility of the charge-separated state. In addition, bis(phenylethynyl)pyrene [38] and bis(phenylethynyl)anthracene-phenothiazine dyads [72] were shown to display a long-lived photoinduced charge separation in the inverted Marcus region. According to the UV/Vis characteristics (additive behavior of donor and acceptor absorptions), donor and acceptor are electronically decoupled in the ground state; however, the quenching of the inherent fluorescence of pyrene or anthracene can be attributed to a photo-induced electron transfer from phenothiazine to the corresponding hydrocarbon acceptor as shown by flash photolysis.

Here we representatively report the rapid Ugi 4CR synthesis of phenothiazine-aromatic hydrocarbon acceptor dyads with anthracen-9-yl, pyren-3-yl, and perylen-1-yl ligation as prototypical systems. In addition, comprehensive physical organic studies of electronic and electrochemical properties investigated by steady-state UV/Vis and fluorescence spectroscopy as well as cyclic voltammetry and DFT computations are reported. The obtained data are interpreted in the light of the Weller approximation to estimate the probability for charge separation by photo-induced electron transfer based upon its Gibbs energy calculated from the analytical data and donor-acceptor distances of lowest energy conformers.

Results and Discussion

Synthesis and structure

The Ugi 4CR synthesis of the three phenothiazine-aromatic hydrocarbon acceptor dyads was performed in analogy to our previously published protocol [71]. The most favorable solvent for Ugi 4CR is methanol, however, portions of dichloromethane were added to increase the solubility and to assure a homogeneous solution. For liberating the free base from the methylamine hydrochloride 1, prepared from the corresponding cyano compound [73] by reduction with lithium aluminium hydride in diethyl ether [74], potassium hydroxide was employed as a base [75]. Successively, the aromatic hydrocarbon carbaldehydes 2, acetic acid (3), and tert-butyl isocyanide (4) were added to the reaction mixture, and after stirring at room temperature for one day the corresponding phenothiazine-aromatic hydrocarbon acceptor dyads 5 were isolated in good to excellent yields (Scheme 1).

Mechanistically, the primary amine 6 generated from methylamine hydrochloride (1) by deprotonation reacts with the aromatic hydrocarbon aldehyde 2 to furnish the imine 7 (Scheme 2), which is protonated by acetic acid (3) to give in equilibrium the iminium ion 8 according to the generally accepted mechanistic rationale for Ugi reactions [67, 68]. The isonitrile 4 attacks the iminium ion 8 to generate the nitrilium ion 9, which in turn reacts with the acetate counter ion to give the acetyl imidate 10. This intermediate finally undergoes an intramolecular acetyl transfer reaction, generally known as the Mumm rearrangement. The ultimate driving force of the Ugi 4CR is the generation of two amide bonds.

The appearance of single signal sets in the $^1$H and $^{13}$C NMR spectra of 5 unambiguously supports the structural assignment and shows that isomer mixtures due to restricted amide bond rotation can be excluded. Distinct resonances in the aromatic region of the spectra account for 9-anthracenyl, 3-pyrenyl, and 1-perylenyl substitutions, respectively. Mass spectrometry and combustion analysis are also in agreement with the structures of phenothiazine-aromatic hydrocarbon acceptor dyads 5.

The conformational mobility of the dyads is largely restricted due to two rigid amide bonds. Therefore, quantum chemical computations [76] both on a semiempirical (PM3) and on a density-functional
Scheme 1. Ugi 4CR synthesis of phenothiazine-aromatic hydrocarbon acceptor dyads 5.

Table 1. Calculated equilibrium geometries on the PM3 and DFT level [76] of the syn- and anti-conformations of the phenothiazine-aromatic hydrocarbon acceptor dyads 5, and intramolecular donor-acceptor distances $d_{\text{Do-Acc}}$.

<table>
<thead>
<tr>
<th></th>
<th>PM3a</th>
<th>DFTb</th>
<th>Distance $d_{\text{Do-Acc}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>syn-5a</td>
<td>96.933</td>
<td>69.13</td>
<td>-2263.09495 -2263.10177 5.51</td>
</tr>
<tr>
<td>anti-5a</td>
<td>105.165</td>
<td>77.87</td>
<td>-2263.08128 -2263.08803 9.03</td>
</tr>
<tr>
<td>$\Delta G($syn-5a – anti-5a$)$</td>
<td>-8.23</td>
<td>-8.74</td>
<td>-0.01368 (-35.90)$^c$</td>
</tr>
<tr>
<td>$K_{\text{syn-5a/anti-5a}}$</td>
<td>27.7</td>
<td>34.0</td>
<td>1.96 $\times 10^6$</td>
</tr>
<tr>
<td>syn-5b</td>
<td>85.14</td>
<td>51.76</td>
<td>-2339.34634 -2339.34606 6.11</td>
</tr>
<tr>
<td>anti-5b</td>
<td>89.96</td>
<td>57.84</td>
<td>-2339.33768 -2339.34606 9.04</td>
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<tr>
<td>$\Delta G($syn-5b – anti-5b$)$</td>
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<td>-6.08</td>
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<tr>
<td>$K_{\text{syn-5b/anti-5b}}$</td>
<td>7.00</td>
<td>11.6</td>
<td>9.5 $\times 10^3$</td>
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<tr>
<td>syn-5c</td>
<td>265.64</td>
<td>226.30</td>
<td>-2724.03876 -2724.04677 7.68</td>
</tr>
<tr>
<td>anti-5c</td>
<td>268.72</td>
<td>225.74</td>
<td>-2724.04075 -2724.04900 13.92</td>
</tr>
<tr>
<td>$\Delta G($syn-5c – anti-5c$)$</td>
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<td>0.56</td>
<td>0.00199 (5.2)$^c$</td>
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<tr>
<td>$K_{\text{syn-5c/anti-5c}}$</td>
<td>3.47</td>
<td>0.80</td>
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<table>
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<th></th>
<th>gas phase in water$^d$</th>
<th>gas phase in water$^d$</th>
<th>Distance $d_{\text{Do-Acc}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>syn-5a</td>
<td>96.933</td>
<td>69.13</td>
<td>-2263.09495 -2263.10177 5.51</td>
</tr>
<tr>
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</tr>
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<td>$K_{\text{syn-5a/anti-5a}}$</td>
<td>27.7</td>
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<td>268.72</td>
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<td>-2724.04075 -2724.04900 13.92</td>
</tr>
</tbody>
</table>

level of theory (DFT, B3LYP functional, 6-31 G* basis set) were performed with the dyads 5 to conduct a global conformational analysis (Table 1, Figs. 2 – 4). For simplification the hexyl substituents of the real compounds 5 were truncated to ethyl substituents. With the exception of dyad 5c the syn-orientation of the phenothiazine and the hydrocarbon acceptor moieties are the energetically preferred conformations, and the calculated Boltzmann distributions based upon the DFT energies clearly underline the dominance of the electronic structure in this interaction. In addition the computed intramolecular distances of donor and acceptor moieties reveal significant differences between the two conformers. Al-
though for dyad 5c the anti-conformation is preferred (see Table 1), the energy differences are small enough to assume a significant contribution of the syn-conformation, which, of course, is most relevant for the distance-dependent efficiency of the photo-induced intramolecular electron transfer (vide infra).

Electronic properties and electronic structure

The electronic ground state properties of the three dyads 5 were studied by cyclic voltammetry and UV/Vis and fluorescence spectroscopy to investigate the excited state (Table 2). Compound 11 [71] (Fig. 5) was employed as a donor reference and the hydrocarbons anthracene [77], pyrene [77], and perylene [78, 79] as acceptor references.

The cyclic voltammograms were recorded at scan rates \( \nu \) of 100, 250, 500, and 1000 mV s\(^{-1}\), and the differences of anodic and cathodic peak potentials were plotted against \( \sqrt{\nu} \) for extrapolating the half-wave potentials \( E_{1/2} \) for a scan rate \( \nu = 0 \) mV s\(^{-1}\) assuming an ideal Nernstian behavior. (For irreversible oxidations the oxidation peak potential was extrapolated for a scan rate \( \nu = 0 \) mV s\(^{-1}\).) In the cyclic voltammograms of the phenothiazine-aromatic hydrocarbon acceptor dyads 5, typical for phenothiazine derivatives [40, 41, 80], first reversible oxidations \( E_{1/2}^{0/+1} \) between 630 and 690 mV are found, and in addition second oxidation waves \( E_{1/2}^{1/+2} \) are found at 1440 (5a) and 1470 mV (5b) as irreversible oxidations, and one at 990 mV (5c) with Nernstian behavior. The direct comparison of the dyads 5 with N-hexyl phenothiazine \( E_{1/2}^{0/+1} = 730 \) mV as a reference clearly indicates that

Scheme 2. Mechanistic rationale for the formation of the dyads 5 by Ugi 4CR.
Fig. 2 (color online). DFT-calculated (B3LYP, 6-31G*) differences of the electronic energies in water according to the SM5.4/P solvation model of the conformers of phenothiazine-anthracene dyad $5a$, donor-acceptor distances $d_{Do-Acc}$, and anti-syn equilibrium ($\Delta G$ and $K$) at room temperature.

Fig. 3 (color online). DFT-calculated (B3LYP, 6-31G*) differences of the electronic energies in water according to the SM5.4/P solvation model of the conformers of phenothiazine-pyrene dyad $5b$, donor-acceptor distances $d_{Do-Acc}$, and anti-syn equilibrium ($\Delta G$ and $K$) at room temperature.

Fig. 4 (color online). DFT-calculated (B3LYP, 6-31G*) differences of the electronic energies in water according to the SM5.4/P solvation model of the conformers of phenothiazine-perylene dyad $5c$, donor-acceptor distances $d_{Do-Acc}$, and anti-syn equilibrium ($\Delta G$ and $K$) at room temperature.

The proximity of the electron donating hydrocarbon moieties shifts their phenothiazine-centered oxidation potential cathodically, i.e. to lower potentials. The second oxidations can be readily assigned to oxidations on the hydrocarbon moieties by comparison with the cyclic voltammograms of anthracene, pyrene and perylene. This similarity of the cyclic voltammograms of the dyads 5 and the reference systems $N$-hexyl phe-
Table 2. Selected electronic properties of the phenothiazine-aromatic hydrocarbon acceptor dyads 5 (oxidation potentials\(^a\), absorption maxima\(^b\), and residual emission maxima\(^c\), Stokes shifts\(^d\)), N-hexyl phenothiazine, anthracene, pyrene, and perylene (oxidation potentials\(^a\), absorption\(^b\) and emission maxima\(^c\), Stokes shifts\(^d\)). Literature references are given in brackets.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxidation potentials(^a)</th>
<th>Absorption(^b)</th>
<th>Emission(^c)</th>
<th>Stokes shift(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(E_{1/2}^{0+/1}) (mV)</td>
<td>(\lambda_{\text{max,abs}}) (nm)</td>
<td>(\lambda_{\text{max,em}}) (nm)</td>
<td>(\Delta\nu) (cm(^{-1}))</td>
</tr>
<tr>
<td>5a</td>
<td>680</td>
<td>259 (207), 308 sh (7), 319 (7), 336 (7), 355 (8), 374 (9), 394 (7)</td>
<td>435(^{c})</td>
<td>2400</td>
</tr>
<tr>
<td>5b</td>
<td>630(^f)</td>
<td>245 (67), 259 (40), 266 sh (39), 279 (36), 318 (15), 332 (27), 348 (33)</td>
<td>425(^f)</td>
<td>5200</td>
</tr>
<tr>
<td>5c</td>
<td>690</td>
<td>258 (51), 294 (7), 301sh (6), 400 sh (11), 422 (24), 448 (30)</td>
<td>465(^{c})</td>
<td>800</td>
</tr>
<tr>
<td>11 [23]</td>
<td>730</td>
<td>259 (39), 311 (6)</td>
<td>450(^a)</td>
<td>9900</td>
</tr>
<tr>
<td>Anthracene</td>
<td>1430 (irr)</td>
<td>251 (97.7), 356 (6.5), 375 (5.8) [77](^f)</td>
<td>385, 405, 430, 455 [77](^f)</td>
<td>700</td>
</tr>
<tr>
<td>Pyrene</td>
<td>1480 (irr)</td>
<td>239 (51.3), 252 (10.7), 261 (19), 272 (30.2), 319 (22.4), 334 (33.1) [77](^f)</td>
<td>375, 385, 395, 420, 445 [77](^f)</td>
<td>3300</td>
</tr>
<tr>
<td>Perylene</td>
<td>1010</td>
<td>254 (34.9), 391 (11.9), 412 (26.8), 439 (35.2) [78, 79](^f)</td>
<td>446, 474, 503 [78, 79](^f)</td>
<td>400</td>
</tr>
</tbody>
</table>

\(^a\) Obtained from cyclic voltammetry in CH\(_2\)Cl\(_2\) at room temp (Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode, obtained at scan rates of \(v = 100, 250, 500, 1000\) mV s\(^{-1}\), N(n-Bu\(_4\))PF\(_6\) as an electrolyte, \(c_0 = 0.1 \text{ mol L}^{-1}\), vs. Fe/Fe\(_{3+}\)); \(^b\) recorded in CH\(_2\)Cl\(_2\) at room temp (\(c_0 = 10^{-3} \text{ mol L}^{-1}\)); \(^c\) recorded against decamethylferrocene (\(E_{1/2} = -0.1\) mV) as a standard; \(^d\) \(\Delta\nu = 1/\lambda_{\text{max,abs}} - 1/\lambda_{\text{max,em}}\) (cm\(^{-1}\)); \(^e\) \(\lambda_{\text{exc}} = 394\) nm; \(^f\) recorded against decamethylferrocene (\(E_{1/2} = -0.1\) mV) as a standard; \(^\ddagger\) \(\lambda_{\text{exc}} = 348\) nm; \(^\circ\) \(\lambda_{\text{exc}} = 448\) nm; \(^\ddagger\) \(\lambda_{\text{exc}} = 311\) nm; \(^\ddagger\) recorded in chloroform; \(^\ddagger\) \(\lambda_{\text{exc}} = 375\) nm; \(^\ddagger\) \(\lambda_{\text{exc}} = 335\) nm; \(^\ddagger\) \(\lambda_{\text{exc}} = 440\) nm.

The inspection of the absorption spectra of the dyads 5 reveals in a first approximation an additive behavior of the absorption bands and of the intensities of the constituting chromophores N-hexyl phenothiazine and anthracene, pyrene or perylene, respectively. A similar additivity was already observed for the phenothiazine-anthraquinone dyad (Fig. 1) [71]. Red-shifted deviations of the absorption maxima and hypochromicity of some bands can be readily rationalized by the difference of the solvation shell of the dyads in comparison to the individual constituents. This additive behavior in the absorption spectra, reflecting ground state characteristics, also suggests that the phenothiazine donor and the hydrocarbon acceptor moieties are electronically decoupled in the electronic ground state.

Most remarkably, as also in the case of the phenothiazine-anthraquinone dyad (Fig. I), a pronounced quenching of the inherent fluorescence of the hydrocarbon donor can be observed, which can be detected only as residual acceptor luminescence for the dyads 5a and 5b, and as an attenuated perylene emission by steady-state emission spectroscopy (Fig. 6 – 8). While the residual emissions of the dyads 5a and 5b display broad unstructured bands, the vibrational fine

Fig. 5. Phenothiazinyl acetyl carboxamide 11 as a donor reference.

Phenothiazine, anthracene, pyrene, and perylene clearly shows that the phenothiazine and the hydrocarbon moieties are essentially electronically decoupled in the electronic ground state. Therefore, the electronic effects should behave additively in the electronic ground state, i.e. as if the phenothiazinyl and hydrocarbon moieties were placed at large distances.
accounts for a small fluorescence quantum yield Φ394 nm). e
E401 nm), 32 and (nm) = Φ298 K, Φ∆− = E(∆−2 = 5aR E(eV)
5a
5b
5c
accounts for a small fluorescence quantum yield Φ394 nm). e
E401 nm), 32 and (nm) = Φ298 K, Φ∆− = E(∆−2 = 5aR E(eV)
5a
5b
5c
structure of dyad 5c, and the narrow Stokes shift, indicate that the remaining emission clearly stems from the perylenyl moiety. The phenothiazine only reference 11 accounts for a small fluorescence quantum yield Φ1 of 0.01 [71]. The relative quantum yields ΦDo-Acc of the dyads 5 were determined at identical concentrations to give values of 0.02 for 5a and 5b, and of 0.24 for dyad 5c. In comparison to anthracene (Φ1 = 0.36 in cyclohexane), pyrene (Φ1 = 0.32 in cyclohexane), and perylene (Φ1 = 0.94 in cyclohexane) [81] the inherent hydrocarbon donor emission is attenuated by factors of 18, 16, and 3.9, respectively. This attenuation is smaller than in the case of the previously reported phenothiazine-anthraquinone dyad (Fig. 1). Therefore, besides PET also energy transfer can contribute as an intermolecular depopulation process in the excited state. Therefore, in the light of the Weller approximation an estimate of the Gibbs energy for the PET was calculated from the analytical data and from the donor-acceptor distances of lowest energy conformers (Table 3) [82]. For this approximation, where the phenothiazinyl moiety acts as a reductive quencher, the reduction potentials of anthracene (E1/2 = −1.97 V, against SCE in acetonitrile), pyrene (E1/2 = −2.04 V, against SCE in acetonitrile), and perylene E1/2 = −1.66 V, against SCE in acetonitrile) [32] were employed.

The Weller approximation of the Gibbs energy for the PET, ΔGET, furnishes negative values in all three cases, i.e. the photo-induced electron transfer from phenothiazine to the luminescent aromatic hydrocarbon acceptor moieties as a driving force for the pronounced emission quenching in the dyad is an exergonic process. Although the crude estimation of the simple free enthalpy of electron transfer ΔGET,simpl calculated from electrochemical and spectral data already
indicates exothermic processes, the term for correction for solvent polarity \( \Delta G_{solv}' \) accounts for a considerable control of the overall magnitude of the PET, and therefore, it also can be fine-tuned to some extent.

Interestingly, the DFT computations (B3LYP functional, basis set 6-31G*) [76] have clearly shown that the coefficient density of the HOMOs is almost completely localized on the phenothiazine unit for the dyads 5a (Fig. 9) and 5b (Fig. 10) and on the perylene core for the dyad 5c (Fig. 11). The HOMO–1 of 5c is localized on the phenothiazine instead (Fig. 11). At first sight this latter finding appears to contradict the electrochemically determined phenothiazine-centered first oxidation (Table 2), which occurs at significantly lower potentials than expected for perylene. However, phenothiazine oxidations are better rationalized on the basis of the thermodynamic stability of the resulting radical cation than by Koopman’s theorem, assuming that the energy of an orbital does not change upon ionization [83]. However, the LUMOs unequivocally reside on the aromatic hydrocarbon cores, supporting the electronic decoupling of the donor and the acceptor in the electronic ground state. It is also noteworthy to mention that the computed HOMO-LUMO gaps of the dyads 5 in vacuum with values of 3.14 (5a, exp. 3.09 eV), 3.31 (5b, exp. 3.37 eV), and 2.97 eV (5c, exp. 2.72 eV) are in a remarkably good agreement with the experimentally determined excitation energies \( E_{00} \). The HOMO–1-LUMO gap of dyad 5c is computed as 3.25 eV and lies in the same order of magnitude than the excitation of phenothiazine in the reference system 11 (3.38 eV). The absorption characteristics of phenothiazine dyads can be easily red-shifted by suitable acceptors and, therefore, charge separation by PET may eventually be possible with visible light by chromophores with lower HOMO-LUMO gaps.

**Conclusion**

The Ugi four-component reaction opens a rapid, modular approach to phenothiazine-aromatic hydrocarbon dyads in good yield. Cyclic voltammetry and UV/Vis spectroscopy clearly indicate an electronic decoupling of the donor and the acceptor substituents in the electronic ground state, while the emission of the aromatic hydrocarbon moieties is efficiently quenched by reductive photo-induced electron transfer from the phenothiazinyl moiety according to static fluorescence
spectroscopy. This scenario is additionally supported by calculating the Gibbs free energies of the PET into the charge-separated states applying the Weller approximation to the absorption and cyclovoltammetric data. This semiquantitative evaluation can be readily applied to optimize photo-induced charge-separation systems which are readily accessible by multicomponent reactions. Studies directed towards multicomponent syntheses of complex light harvesting and charge separation systems are currently underway.

Experimental Section

General information

Commercial grade reagents were used as supplied without further purification and were purchased from abcr, Acros Organics, Alfa Aesar, and Sigma-Aldrich Chemie. The purification of Ugi compounds 5 was performed by column chromatography on silica gel 60 M (0.04–0.063 mm) from Macherey-Nagel using flash technique under pressure of 2 bar. The crude mixtures were adsorbed on Celite® 545 from Carl Roth before chromatographic purification. The reaction progress was monitored qualitatively using TLC Silica gel 60 F254 aluminum sheets obtained from Merck, Darmstadt. The spots were detected with UV light at 254 nm and using an iodine chamber.

1H, 13C, and 135-DEPT 13C NMR spectra were recorded on Bruker Avance DRX 300 and Bruker Avance DRX 500 spectrometers. CD2Cl2 and [D6]acetone were used as deuterated solvents. The resonances of the solvents were locked as internal standards (δ in ppm in CD2Cl2: 1H 5.32, 13C 54.0; CD3COCD3: 1H 2.05, 13C 29.92 ppm). The multiplicities of the signals were abbreviated as follows: s: singlet; d: doublet; dd: doublet of doublets; t: triplet; m: multiplet. The type of carbon nucleus was determined on the basis of 135-DEPT 13C NMR spectra. For the description of the 13C NMR spectra primary carbon nuclei are abbreviated with CH3, secondary carbon nuclei with CH2, tertiary carbon nuclei with
CH, and quaternary carbon nuclei with C<sub>quat</sub>. MALDI mass spectra were measured on a Bruker Ultraflex spectrometer, ESI mass spectra were measured on an Ion-Trap-API mass spectrometer of Finnigan LCQ Deca (Thermo Quest). IR spectra were obtained on a Bruker Ultraviolet spectrometer, and UV spectra were measured on a Perkin Elmer Series II Analyzer 2400 in the Microanalytical Laboratory of the Institut für Pharmazeutische und Medizinische Chemie der Heinrich-Heine-Universität Düsseldorf. Cyclic voltammetry experiments were performed with a 263A E&G Princeton Applied Research device as potentiostatic instrumentation under argon in dry and degassed dichloromethane at T = 298 K and at scan rates of 100, 250, 500 and 1000 mV s<sup>−1</sup>. The electrolyte was tetrabutylammonium hexafluorophosphate at a concentration of C<sub>0</sub> = 0.1 mol L<sup>−1</sup>. The working electrode was a 1 mm platinum disc, the counter electrode was a platinum wire and the reference electrode was a silver/silver chloride electrode filled with aqueous saturated sodium chloride solution. The potentials were calibrated using [FeCp<sub>2</sub>]−/[FeCp<sub>2</sub>]<sup>2+</sup> (E<sub>0</sub>/2+ = 450 mV) [84] as an internal potential standard.

**Synthesis of compounds 5 via Ugi four-component reaction (general procedure)**

In a 25 mL Schlenk tube 1.0 equiv. of (10-hexyl-10H-phenothiazin-3-yl)methanamine hydrochloride (1) [74] was dissolved in methanol (2 mL) and 1.0 equiv. of potassium hydroxide (28 mg, 0.50 mmol) was added, and the mixture was stirred for 30 min at r.t. (for experimental details see Table 4). 1.0 equiv. of aldehyde 2 was added neat or as a dichloromethane solution, and the solution was stirred at r.t. for 1 h, followed by the addition of 1 equiv. of acetic acid (3) and 1 equiv. of tert-butyl isocyanide (4) by syringe. The reaction mixture was stirred overnight at r.t. The solvents were removed in vacuo, and the crude product was purified by column chromatography on silica gel to give the analytically pure Ugi products 5.

<table>
<thead>
<tr>
<th>Entry</th>
<th>(10-Hexyl-10H-phenothiazin-3-yl)methanamine hydrochloride (1)</th>
<th>KOH</th>
<th>Aldehyde 2</th>
<th>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Acetic acid (3)</th>
<th>tert-Butyl isocyanide (4)</th>
<th>Ugi 4CR products 5 (yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>175 mg (0.50 mmol)</td>
<td>28 mg (0.5 mmol)</td>
<td>103 mg (0.50 mmol) of 2a [85]</td>
<td>1 mL</td>
<td>30 mg (0.5 mmol)</td>
<td>42 mg (0.5 mmol)</td>
<td>281 mg of 5a (87%)</td>
</tr>
<tr>
<td>2</td>
<td>175 mg (0.50 mmol)</td>
<td>28 mg (0.5 mmol)</td>
<td>115 mg (0.50 mmol) of 2b [86]</td>
<td>–</td>
<td>30 mg (0.5 mmol)</td>
<td>42 mg (0.5 mmol)</td>
<td>225 mg of 5b (67%)</td>
</tr>
<tr>
<td>3</td>
<td>87.2 mg (0.25 mmol)</td>
<td>14.0 mg (0.25 mmol)</td>
<td>89.1 mg (0.25 mmol) of 2c [87]</td>
<td>1 mL</td>
<td>15 mg (0.25 mmol)</td>
<td>21 mg (0.25 mmol)</td>
<td>114 mg of 5c (56%)</td>
</tr>
</tbody>
</table>

Table 4. Experimental details for the synthesis of the Ugi products 5.
N-(tert-Butyl)-2-(N-(10-hexyl-10H-phenothiazin-3-yl)methyl)acetamido)-2-(pyren-3-yl)acetamide (5b)

After recrystallization from ethanol 225 mg (67%) of compound 5b were obtained as a yellow solid, m.p. 127 – 130 °C. Rf (n-hexane-ethyl acetate 2 : 1) = 0.19. – 1H NMR (300 MHz, CDCl3): δ = m 7.05 (t, J = 7.4 Hz, 1 H), 7.03 (t, J = 7.0 Hz, 1 H), 7.31 (s, 1 H), 7.94 (d, J = 2.0 Hz, 1 H), 8.02 (d, J = 7.6 Hz, 1 H), 8.08 (d, J = 7.9 Hz, 1 H), 8.11 – 8.20 (m, 3 H), 8.20 – 8.26 (m, 3 H). – 13C NMR (75.5 MHz, CDCl3): δ = m 43.1 (CH3), 23.3 (CH2), 26.9 (CH2), 27.1 (CH2), 29.0 (CH3), 32.1 (CH2), 47.4 (CH2), 50.1 (CH2), 51.9 (Cquat), 58.1 (CH), 114.6 (CH), 116.0 (CH2), 122.7 (CH), 123.8 (Cquat), 124.4 (CH), 124.7 (Cquat), 125.2 (Cquat), 125.29 (CH), 125.32 (Cquat), 125.4 (CH), 125.6 (CH), 126.4 (CH), 126.5 (CH), 127.0 (CH), 127.6 (CH), 127.9 (CH), 127.96 (CH), 128.01 (CH), 128.6 (CH), 129.1 (CH), 131.5 (Cquat), 131.65 (Cquat), 131.69 (Cquat), 132.0 (Cquat), 132.3 (Cquat), 133.0 (Cquat), 143.5 (Cquat), 145.5 (Cquat), 171.2 (Cquat), 171.9 (Cquat). – MS (MALDI): m/z = 667.3 [M]+. – IR: ν (cm−1) = 3285 (w), 3049 (w), 2957 (w), 2926 (w), 2855 (w), 1682 (m), 1624 (s), 1543 (m), 1497 (w), 1464 (s), 1443 (m), 1420 (m), 1404 (m), 1364 (m), 1314 (m), 1283 (m), 1242 (s), 1224 (m), 1184 (m), 1158 (w), 1105 (w), 1053 (w), 1034 (w), 978 (w), 970 (w), 943 (w), 843 (s), 826 (m), 818 (m), 800 (m), 789 (m), 745 (s), 714 (m), 683 (m), 644 (m), 623 (m). – UV/Vis (CH2Cl2): λmax (ε) (nm) = 258 (51 000), 294 (7000), 301sh (6000), 400sh (11 000), 422 (24 000), 448 (30 000). Anal. for C33H32N2O2S: calcd. C 77.33, H 6.79, N 6.29; found C 77.15, H 6.61, N 6.02.

Acknowledgement

The support of this work by the Fonds der Chemischen Industrie and the Jürgen Manchot Stiftung (scholarship for S. B.) is gratefully acknowledged.


[74] As implemented in SPARTAN ’08 (V 1.2.0), Wavefunction Inc., Irvine, CA (USA), 2008.
[84] Aldehyde 2c was synthesized by standard Suzuki coupling (K$_2$CO$_3$, 3 mol-% Pd(PPh$_3$)$_4$, in DME-H$_2$O 2 : 1 at 100 °C for 22 h) of 1-bromoperylene (Patent US2011/15440, A1, 2011) and 4-formyl-phenylboronic acid in 75 % yield.