

Photocatalytically Active Materials with Pyridinium-enolate Partial Structures

Andreas Schmidt and Marcel Albrecht

Clausthal University of Technology, Institute of Organic Chemistry, Leibnizstraße 6,
D-38678 Clausthal-Zellerfeld, Germany

Reprint requests to Priv.-Doz. Dr. rer. nat. habil. Andreas Schmidt. Fax: +49(0)5323-722858.
E-mail: schmidt@ioc.tu-clausthal.de

Z. Naturforsch. **2008**, 63b, 465–472; received January 8, 2008

2,3-Dichloro-1,4-naphthoquinone and tetrabromo- or tetrachloro-1,4-benzoquinone were converted into pyridinium enolate betaines by reaction with pyridine or 4,4'-bipyridine. The reaction conditions were applied to poly-(4-vinylpyridine) and a modified Merrifield resin to obtain functionalized polymeric materials. These were examined in thermogravimetric analyses. Reversible photocatalytic electron transfer reactions in the presence of proflavinium and EDTA as sensitizer and sacrificial donor, respectively, were examined. All monomeric and polymeric materials, except for one, proved to be active.

Key words: Mesomeric Betaines, Radicals, Electron Transfer Reactions, Photocatalysis

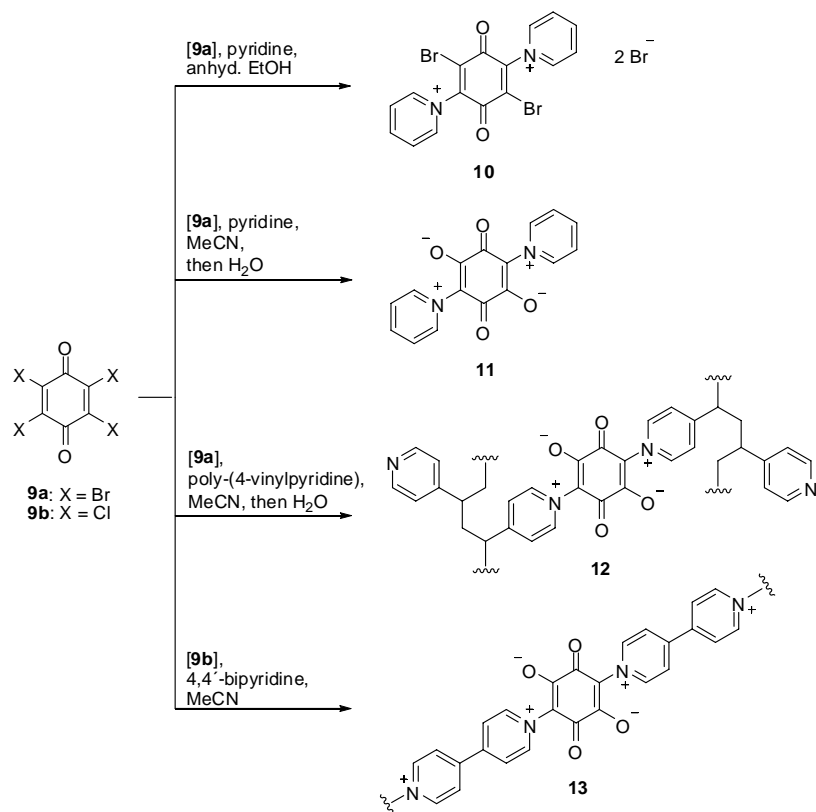
Introduction

In heterocyclic mesomeric betaines an even number of charges is delocalized within a common π -electron system. In 1985 four distinct types of heterocyclic mesomeric betaines were classified, *i. e.* conjugated mesomeric betaines (CMB), cross-conjugated mesomeric betaines (CCMB), pseudo-cross-conjugated mesomeric betaines (PCCMB), and ylides which form a subclass of CMB [1]. By recognition of the type of conjugation of a mesomeric betaine its chemical properties can be predicted. For example, numerous 1,3-dipoles which are used in natural product synthesis [2] are conjugated mesomeric betaines. Cross-conjugated mesomeric betaines undergo 1,4-dipolar cycloadditions which were also applied in interesting heterocyclic [3] or natural product syntheses [4]. Very recently it was realized that pseudo-cross-conjugated mesomeric betaines can be converted into Arduengo carbenes by extrusion of heterocumulenes [5] and *vice versa* [6]. In view of recent progress in material sciences, CMB such as pyridinium-olates and isoquinolinium-3-olates [7] as well as cross-conjugated systems such as pyrimidinium-olates [8] are photosensitive moieties of polymeric materials, as polarities, refractive indices and densities of such materials change on irradiation. The formation of radical species from mesomeric betaines, however, has neither been exam-

ined from the viewpoint of organic synthesis, nor from the viewpoint of material sciences, although much interest has been focussed on functional groups and ring systems including pyridines [9] and bipyridines [10] as potential radical partial structures of new materials. Some multifunctional spin systems such as photochromic radicals have also been developed [11].

Recently, we examined the alkaloid **1** from *Punica granatum* L. [12] as well as derivatives [13]. The natural product forms the mesomeric betaines **2A** and **2B** in equilibrium ("Punicin," Scheme 1) [12]. Interestingly, the betaine **2A** belongs to the class of conjugated mesomeric betaines (CMB), whereas its tautomer **2B** is a member of the class of cross-conjugated mesomeric betaines (CCMB). At higher pH values, deprotonation to the monoanionic species **3** or pericyclic ring cleavage to **4** occurs. Moreover, Punicin possesses oxidizing (pyridinium) and reducing (benzene-1,4-diolate) partial structures. Internal electron transfers, *i. e.* disproportionation, resulted in diradicals **2^{2•}**, whereas an intermolecular redox reaction gave a radical anion **2^{•-}** and a radical cation **2^{•+}**, or its tautomers. We performed EPR spectroscopy at X as well as W band and DFT computations, and characterized radical species formed from Punicin and some polymeric derivatives [14].

We wish to report here our results on the synthesis of new materials containing enol pyridinium betaine

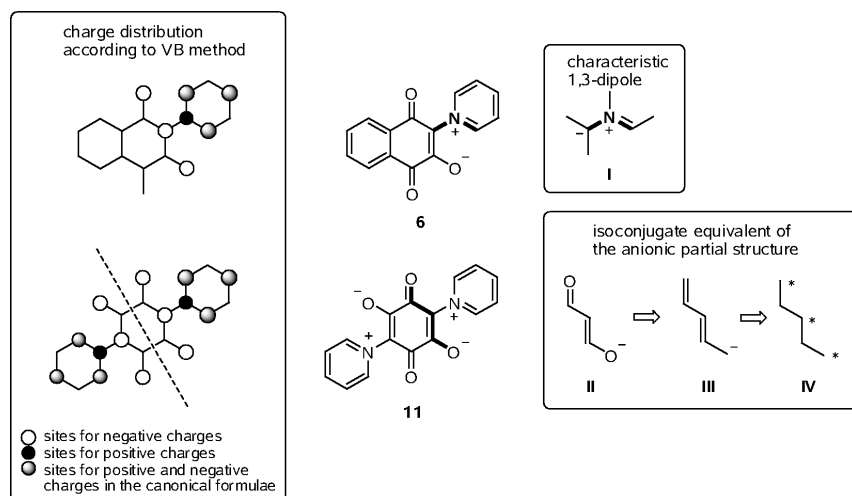


Scheme 3.

istic bands of the unreacted starting materials. Thus, the $\text{O}=\text{C}-\text{C}=\text{C}-\text{C}=\text{O}$ vibration of the polymeric material could unambiguously be assigned to a band at 1545 cm^{-1} in the IR spectrum. As expected, the ^1H NMR signals are broad and unresolved so that the degree of substitution cannot be determined by this spectroscopic method. The nitrogen content (6.11 %) reveals that 50 % to 75 % of the pyridine rings of the poly-(4-vinylpyridine) are substituted. As examples, calculated values of completely and 50 % substituted polymers are 5.05 % and 7.07 %, respectively. Polymer **7**, however, includes small amounts of THF and water of crystallization as evidenced by thermogravimetric analyses (*vide infra*), so that the elemental analyses gave only approximate values for the degree of substitution. A 4,4'-bipyridinium functionalized Merrifield resin, which we described earlier [14], was reacted with 2,3-dichloro-1,4-naphthoquinone in acetic acid to give a new material which is represented by the idealized structure **8** (Scheme 2). Cross-linked substructures in the starting material are omitted for the sake of clarity. These resulted from reaction of 4,4'-

bipyridine as a bisnucleophile with two chloromethyl groups of the Merrifield resin. A comparison of the CHN analyses before and after the functionalization with 2,3-dichloro-1,4-naphthoquinone brought some information on the structure of **8**. Thus, the experimentally determined nitrogen content is considerably lower than before (4.74 %) indicative of a reaction between the polymer and 2,3-dichloro-1,4-naphthoquinone, but higher than calculated for a complete substitution of all unsubstituted pyridine rings (4.33 %). The $\text{O}=\text{C}-\text{C}=\text{C}-\text{C}=\text{O}$ vibration was found at 1542 cm^{-1} in the IR spectrum.

Then, perhalogenated 1,4-benzoquinones were converted into new materials and monomeric model compounds (Scheme 3). Thus, tetrabromo-1,4-benzoquinone (**9a**), prepared by a two-step procedure [16], yielded air and moisture sensitive 3,6-dibromo-2,5-di(1-pyridinio)-1,4-benzoquinone (**10**) by reaction with pyridine in anhydrous ethanol. Reaction in acetonitrile and subsequent quenching of the reaction mixture with water resulted in the formation of 2,5-di(1-pyridinio)-1,4-benzoquinone-3,6-diolate (**11**)



Scheme 4.

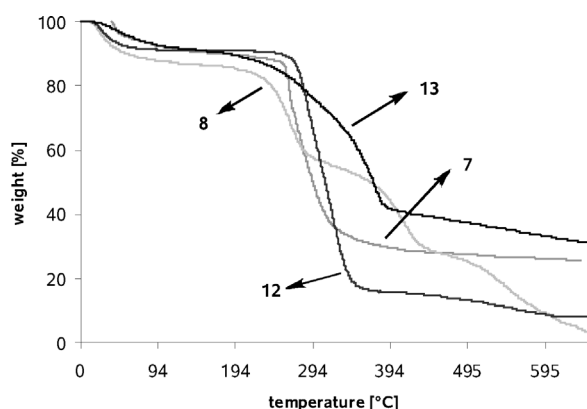


Fig. 1. Thermogravimetric analyses of compounds 7, 8, 12, and 13.

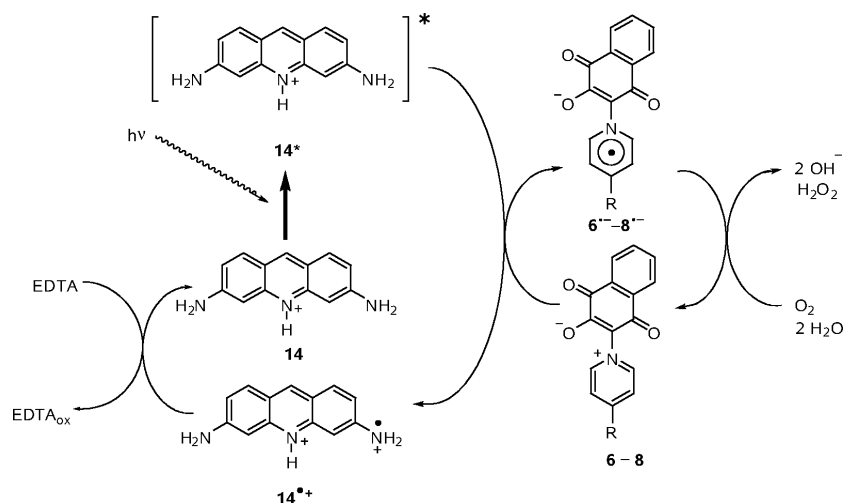
which is orange in color. The characteristic $\text{O} \cdots \text{C} \cdots \text{C} \cdots \text{O}$ vibration band in the IR spectrum is found at 1557 cm^{-1} in this reference material. Under analogous reaction conditions, poly-(4-vinylpyridine) gave a material which displayed an absorption band at 1556 cm^{-1} , and which can be represented by the idealized formula **12**. The nitrogen contents determined by elemental analysis revealed that 50 % of the pyridine rings of the starting polymer were substituted (calcd. 10.57 %; found: 10.45 %). We cannot differentiate, however, between inter- and intramolecular cross-linkings. Tetrachloro-1,4-benzoquinone (**9b**) reacted with 4,4'-bipyridine to the dark brown polymer **13** which displayed a band at 1561 cm^{-1} in the IR spectrum. Once again, conclusions about the structure of this material can be drawn from the elemental analysis, as the nitrogen contents decreases with in-

creasing chain length of the polymer. Thus, the value of the nitrogen contents (found: 7.96 %) hints at a high molecular weight. As example, a structure containing six quinones and seven bipyridinium segments contains 10.27 % of nitrogen. Water of crystallization, a typical phenomenon in the chemistry of heterocyclic mesomeric betaines, prevented us from gaining more information from the elemental analyses.

The thermogravimetric analyses of the new materials are shown in Fig. 1. The weight loss of 8–13 % at temperatures of 60–70 °C and 100–120 °C is due to the extrusion of solvents such as THF, acetone, toluene and water from the polymers, respectively. A considerable decomposition of the materials begins at temperatures above approximately 200 °C. In general, the thermal stability of the substituted polymer **7** is smaller than that of pure poly(4-vinylpyridine). The weight loss of 61 % on heating **7** to 301 °C is caused by extrusion of the naphthoquinone-betaine moiety. The polymer **8** displays three steps of weight loss on heating: At 254 °C the naphthoquinone substituent is extruded (weight loss: 33 %). At 398 °C the 4,4'-bipyridine partial structure is cleaved (weight loss: 27 %), and at 555 °C the cleavage of the polymer backbone can be observed. The polymers **12** and **13** possessing dibetainic structures decompose to unidentifiable products, because extrusion of one component results in the destruction of the polymer backbone.

Classifications

All betaines described here are members of the class of conjugated mesomeric betaines (CMB). Accord-



Scheme 5.

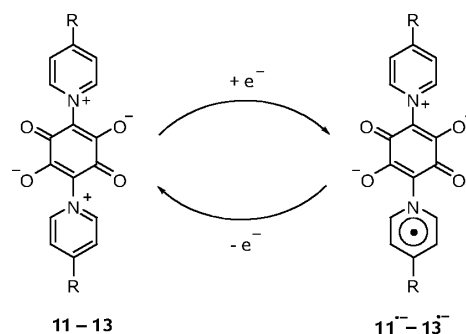
ing to the valence bond approach for the classification, sites for positive and negative charges exist in the canonical formulae which is characteristic for this type of conjugation (Scheme 4). The recognition of characteristic 1,3-dipole increments from the canonical formulae is an alternative method to classify the type of conjugation. In the betaines described here, 1,3-dipole **I** (azomethine ylide) can be dissected from the mesomeric structures which is typical for the class of CMB. Furthermore, the cationic partial structure is joined to the negative partial structure, *i. e.* (*E*)-3-oxo-prop-1-en-1-olate **II**, through a starred position (*cf.* **IV**) of its isoconjugated equivalent hydrocarbon, *i. e.* (*E*)-penta-2,4-dien-1-ide **III**. This is also characteristic for the class of conjugated mesomeric betaines.

Application

We examined the capabilities of the new materials and their monomeric model compounds in coupled photocatalytic electron transfers. We intended to produce radical anions such as **6•- - 8•-** on irradiation of **6-8** in systems consisting of proflavine **14** as sensitizer and EDTA in aqueous solution under an inert atmosphere (Scheme 5).

Likewise, radical anions of the second series of compounds can be postulated to be formed as follows from Scheme 6.

In this cycle the oxidized photocatalyst **14•+** can be regenerated by an electron transfer from the disodium ethylenediamine-tetraacetate (EDTA) which serves as a sacrificial donor. Reoxidation of the radical anions **6•- - 8•-** and **11•- - 13•-**, if formed under these



Scheme 6.

conditions, in the presence of oxygen (air) resulted in the formation of hydroxide ions. This is indicated by an increasing pH value with irradiation time. We therefore first performed a blind probe under analogous reaction conditions without polymers and their model compounds. No change of the pH was observable (Fig. 2). In the presence of **6-8**, **11**, and **12** the color of the solutions or suspensions changed after irradiation within a couple of minutes from yellow to brown, and the original yellow color reconstitutes immediately after exposure to air. This cycle can be started again after rinsing the reaction mixture with nitrogen followed by irradiation and can be repeated numerous times. Stable radical species from viologen [17] or dipunicin derivatives [13] under these conditions are blue or greenish-blue in color and were observed by UV spectroscopy. However, the concentrations of radical species described here are too small for a detection by UV spectrometry. We monitored the reaction by measuring the pH of the solutions or sus-

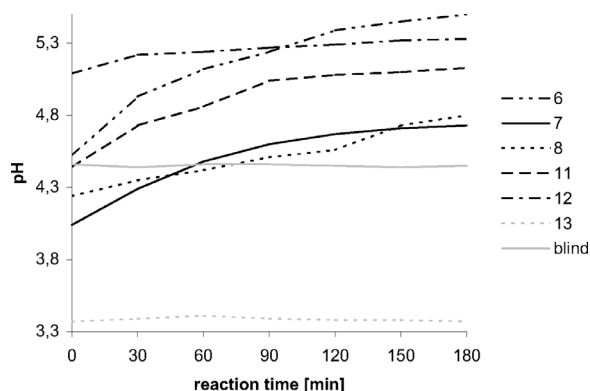


Fig. 2. Change of the pH of monomeric and polymeric materials on irradiation in reversible photocatalytic electron transfers.

pensions during irradiation in the presence of air, and our results are presented in Fig. 2. All compounds described here – except for polymer **13** – obviously are able to undergo these coupled photocatalytic electron transfers and are therefore interesting candidates for technical applications. The best result was achieved by compound **6**, followed by polymers **7** and **11** which cause an increase of the pH value by 0.98 and 0.69, respectively.

In summary, we present new materials possessing partial structures of conjugated heterocyclic mesomeric betaines which are active in reversible photocatalytic electron transfer reactions.

Experimental Section

The ^1H and ^{13}C NMR spectra were recorded on Bruker ARX-400 and DPX-200 spectrometers. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, m = multiplet, b = broad. FT-IR spectra were obtained on a Bruker Vektor 22 in the range of 400 to 4000 cm^{-1} (2.5 % pellets in KBr). A TQ-150 medium-pressure 150 W mercury lamp (UV-Consulting Peschl, Mainz, Germany) in a pyrex photoreactor was used for the irradiation experiments. Poly(4-vinyl-pyridine) [CAS 25232-41-1] was purchased from Sigma Aldrich, [$T_g = 137^\circ\text{C}$; $M_w = 60000$], and Merrifield resin crosslinked with 2 % DVB, 200–400 mesh, from Fluka.

2-(1-Pyridinio)-1,4-naphthoquinon-3-olate (**6**)

2,3-Dichloro-1,4-naphthoquinone (1.14 g, 5 mmol) was dissolved in 50 mL of hot acetic acid. Then pyridine (0.40 mL, 5 mmol) was added. The mixture was heated to 120–130 $^\circ\text{C}$ for 5 h. After the addition of 200 mL of water the resulting solution was extracted with diethyl

ether. The aqueous phase was evaporated, and the resulting solid was filtered off and washed with toluene. Recrystallization from DMSO gave 508 mg (40 %) of an orange solid. M. p. 298–299 $^\circ\text{C}$ (302–303 $^\circ\text{C}$ [15]). – IR (KBr): $\nu = 3424, 1687, 1593, 1557, 1470, 1373, 995, 678\text{ cm}^{-1}$. – $3\text{ C}_{15}\text{H}_9\text{NO}_3 \cdot 2\text{H}_2\text{O}$ (789.20): calcd. C 68.44, H 3.96, N 5.32; found C 68.00, H 3.62, N 5.18.

Polymer **7**

2,3-Dichloro-1,4-naphthoquinone (1.23 g, 5.4 mmol) in 50 mL of acetic acid was added to a solution of poly(4-vinylpyridine) (500 mg) in acetic acid. The mixture was heated to 120–140 $^\circ\text{C}$ for 2 h. The solvent was then removed, and water was added. Evaporation of the solvent gave a red polymer (740 mg) which was dissolved in methanol. This solution was added to THF in which the product precipitated. M. p. 200–210 $^\circ\text{C}$ (decomp.). – ^1H NMR (200 MHz, D_2O): $\delta = 8.41$ (bs), 7.44 (bs), 2.90–1.80 (m, 3H, polymer chain) ppm. – IR (KBr): $\nu = 3419, 1686, 1635, 1588, 1545, 1366, 1230, 996, 821, 553\text{ cm}^{-1}$. – Found C 57.40, H 5.26, N 6.11.

Polymer **8**

2,3-Dichloro-1,4-naphthoquinone (681 mg, 3 mmol) was dissolved in 30 mL of hot acetic acid. Then the 4,4'-bipyridinium-substituted Merrifield resin [14] (300 mg) was added. The suspension was heated at 100 $^\circ\text{C}$ for 5 h. After addition of 50 mL of water the solid was filtered off and washed with hot toluene to give a reddish brown polymer (254 mg). – IR (KBr): $\nu = 3424, 1685, 1634, 1589, 1542, 1361, 1265, 1215, 806, 698\text{ cm}^{-1}$. – Found C 67.43, H 5.22, N 4.74.

3,6-Dibromo-2,5-di(*N*-pyridinio)-1,4-benzoquinone dibromide (**10**) [18]

Tetrabromo-1,4-benzoquinone (840 mg, 2 mmol) was suspended in 30 mL of anhyd. ethanol under a nitrogen atmosphere. After addition of anhyd. pyridine (0.5 mL, 6 mmol) the mixture was heated at reflux temperature for 6 h. Evaporation of the solvent gave a reddish brown solid which proved to be sensitive towards moisture so that the product could not be characterized completely. – ^1H NMR (200 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 8.93$ (d, $J = 5.0\text{ Hz}$, 2H, $\alpha\text{-H}$), 8.58 (t, $J = 7.8\text{ Hz}$, 1H, $\gamma\text{-H}$), 8.06 (dd, $J = 7.8\text{ Hz}$, $J = 6.5\text{ Hz}$, 2H, $\beta\text{-H}$) ppm. – IR (KBr): $\nu = 3061, 1611, 1562, 1474, 1162, 753, 679, 609\text{ cm}^{-1}$.

2,5-Di(*N*-pyridinio)-1,4-benzoquinone-3,6-diolate (**11**) [17]

Tetrabromo-1,4-benzoquinone (840 mg, 2 mmol) was dissolved in 45 mL of hot acetonitrile. Then pyridine (0.65 mL, 8 mmol) was added. The mixture was heated at reflux temperature for 2 h and hydrolyzed with 40 mL of water.

Acetonitrile was evaporated, and the resulting solution was cooled in an ice bath until a precipitate was formed. The solid was filtered off and washed with water. Recrystallization from acetic acid gave 241 mg (41 %) of an orange solid. M. p. > 355 °C. – ^1H NMR (200 MHz, $[\text{D}_6]\text{DMSO}$): δ = 8.77 (dd, J = 6.7 Hz, J = 1.3 Hz, 2H, α -H), 8.54–8.46 (m, 1H, γ -H), 8.10 (t, J = 6.7 Hz, 2H, β -H) ppm. – IR (KBr): ν = 3511, 3459, 3114, 1557, 1467, 1346, 1140, 853, 779, 685, 622 cm^{-1} . – $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (312.07): calcd. C 61.54, H 3.87, N 8.97; found C 61.01, H 3.46, N 8.88.

Polymer 12

To a suspension of poly(4-vinylpyridine) (310 mg) in 30 mL of acetonitrile was added a solution of tetrabromo-1,4-benzoquinone (500 mg, 1.2 mmol) in 15 mL of acetonitrile. After stirring at reflux temperature for 3 h the solvent was removed, and 30 mL of water were added. The solvent was removed, and the resulting precipitate was refluxed with acetone for 30 min. Filtration and washing with acetone gave 273 mg of a dark brown polymer. M. p. 185 °C (decomp.). – IR (KBr): ν = 3424, 1635, 1601, 1556, 1454, 1417, 1220, 1068, 1000, 824 cm^{-1} . – Found C 63.23, H 5.27, N 10.45. NMR spectra could not be measured because of the insolubility of the product in organic solvents.

Polymer 13

A solution of 4,4'-bipyridine (3.90 g, 25 mmol) in 25 mL of acetonitrile was added to a boiling solution of tetrachloro-1,4-benzoquinone (1.53 g, 6.25 mmol) in acetonitrile. The mixture was refluxed for 2 h and then hydrolyzed with 100 mL of water. After cooling the reddish brown precipitate was filtered off and washed with water. Recrystallization from water / formic acid and washing with water and hot toluene gave 920 mg of a dark brown solid. M. p. > 340 °C. – ^1H NMR (200 MHz, $[\text{D}_6]\text{DMSO}$): δ = 8.97 (m, 4H, overlapping signals), 8.62 (d, J = 6.4 Hz, 2H), 8.17 (d, J = 4.9 Hz, 2H) ppm. – IR (KBr): ν = 3427, 1698, 1561, 1337, 814, 735 cm^{-1} . – Found C 55.19, H 2.58, N 7.96.

Coupled photocatalytic electron transfer

100 mg of the polymers and their model compounds, respectively, were dissolved or suspended in a solution of 200 mg of EDTA and 3 mg of proflavine hemisulphate dihydrate in 10 mL of water. The mixture was then irradiated with a UV lamp. During the irradiation aliquots were taken from the solution, and the pH value of these samples was determined with a pH meter.

Acknowledgement

Petra Dröttboom is gratefully acknowledged for performing the TGA experiments.

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