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Diazobenzo[a]fluorene derivatives as visible photosensitizers for free radical polymerization

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ABSTRACT

Several benzophenazine dyes containing a diazobenzo[a]fluorene moiety have been synthesized and characterized by ¹H NMR spectroscopy and mass spectrometry (CI MS). The spectroscopic and electrochemical properties of these dyes were examined. These compounds were evaluated as potential light absorbing chromophores for free radical polymerization. The results are discussed on the basis of the free energy change for electron transfer from the diazobenzo[a]fluorene dyes to the electron donors/acceptors. The kinetic studies of the photoinitiated polymerization of trimethylolpropane triacrylate (**TMPTA**) using electron donors, such as phenylthioacetic acid, phenoxyacetic acid, *N*-phenylglycine and ethyl 4-*N*,*N*dimethylaminobenzoate, and electron acceptors, such as 1-methoxy-4-phenylpyridinium tetrafluoroborate and 1-ethoxy-2-methylpyridinium hexafluorophosphate, have shown that these dyes are efficient photoinitiators for free radical polymerization in visible light. The heavy atoms present in the chemical structure may lead to excited triplet states within the dye facilitating electron transfer from these states.

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PIGMENTS

1. Introduction

Benzophenazine derivatives play an important role in pharmacology and in the chemistry of dyes. These compounds are primarily known for their use as antibacterial agents, antibiotics, fungicides, anticonvulsants, sensitizers for film formers, antioxidants, vat dyes and pigments [1–6]. Although phenazine derivatives are well described, there is little information in the literature [7–9] regarding the synthesis and application of more complex benzophenazine compounds in photochemistry.

In recent years, light induced polymerization has attracted great interest due to the large number of applications in coatings for various materials, adhesives, printing inks and photoresists [10–14] as well as in high-tech domains, optoelectronics, laser imaging, stereolithography because of its low energy consumption and high efficiency [15,16].

Initially, photoinitiating systems sensitive to ultraviolet light were used. However, many attempts have been made to develop efficient photoinitiating polymerization systems that can be activated by visible light, because this light is cheap, safe and exhibits higher penetration compared to ultraviolet light. Visible photoinitiator systems often employ dyes as light absorbing chromophores (photosensitizer) that participate in the photoinduced electron transfer (PET) process leading to the formation of free radicals that initiate polymerization.

Two distinct mechanisms for sensitization are involved depending on the nature of the dye. The first is photoreducible sensitization in which the dye is photoreduced in the presence of a suitable reductant (N-phenylglycine [17], phenylthioacetic acid [18] or alkyltriphenylborane [19,20]). The second type is polymerization initiated via photooxidation of the dye by a strong electron acceptor (*N*-alkoxypyridinium salt [21]). These types of sensitization are used much less often because there are a few reactants that initiate acrylate monomer photopolymerization via an electron transfer process from the excited states of the dyes to pyridinium salts [22]. A new, effective visible light photoinitiating system that possesses specific properties for special applications, such as in dental materials, is still needed. The most popular photoinitiator used in commercially available dental restorative materials is camphorquinone (CQ bornadienone, 1,7,7-trimethylbicyclo(2,2,1)-heptane-2,3-dione), which absorbs light in the region of 200–300 nm ($\varepsilon = 10,000$) and in the visible region of 400–500 nm ($\varepsilon = 40$) [23–25]. The studies of diazobenzo[a]fluorene dyes as an alternate photoinitiator to camphorquinone in dental adhesives is of particular interest.

The main goal of the current study is the synthesis of (1) and (2a-2d), the evaluation of their basic spectroscopic and



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Scheme 1. The structure of the electron donors/acceptors and TMPTA.

electrochemical properties and their application in free radical polymerization as visible photoinitiators of trimethylolpropane triacrylate (**TMPTA**) in the presence of electron donors/acceptors (Scheme 1). In addition, the electron affinity (EA_S) and ionization potential (IP_S) of these compounds are calculated using Density Functional Theory (DFT).

It is well known [26] that the reaction of 2,3-dichloronaphthoquinone with compounds containing a reactive group in the *ortho* position, such as *o*-phenylenediamines or *o*-aminopyridine, yields angular benzo[a]phenazine derivatives, such as compound (1)[27].



The first representative system (**1**) was synthesized by William L. Mosby and Richard J. Boyle in 1959 [27] by refluxing 2,3-dichloro-1,4-naphthoquinone with *o*-aminopyridine in ethanol and in the presence of sodium carbonate. An alternative method of preparing (**1**) involves the condensation of 2,3-dichloro-1,4-naphthoquinone with 2-acetamidopyridine in methyl cellosolve under reflux [28]. The same product was also produced by the reaction of 2-aminopyridine with either 2-acetamido-3-chloro-1,4-naphthoquinone or 3,4-dichloro-1,2-naphthoquinone [27].

The derivatives (**2a**–**2d**) containing different substituents R (CH₃, Cl or Br) were prepared by condensation of (**1**) with the appropriate *o*-phenylenediamine in the presence of acetic acid [28]. The substituents R were selected based on their different electronic properties (+I, +M: CH₃ and -I, +M: halogens), which could potentially affect the position of the dye's absorption band. In

addition, the presence of halogens, especially Br [29–31], stabilizes the triplet state of the dye and facilitates the electron transfer process.



2. Experimental

2.1. General

The trimethylolpropane triacrylate (TMPTA) monomer, electron donors (D1-D4), electron acceptor (A1), 1-methyl-2pyrrolidone and the synthesis reagents for the preparation of the dyes were purchased from Sigma-Aldrich (Poznan, Poland) and POCh (Gliwice, Poland). Compounds (1) and (2a) were synthesized according to the protocol in Ref. [28]. 1,2-Dibromo-4,5-phenylenediamine was synthesized in accordance with Ref. [32]. 1-Ethoxy-2-methylpyridinium hexafluorophosphates (A2) was synthesized according to the procedure described in Ref. [33]. The dyes were identified and characterized by ¹H NMR spectroscopy [Bruker Avance DPX 250, CDCl₃, TMS, δ (ppm), Germany] and chemical ionization mass spectrometry (CI MS) [Finnigan MAT 95 spectrometer, USA] with the application of isobutane. The purity of the dyes was verified using thin-layer chromatography [TLC, Merck Silica gel 60, solvent: toluene/pyridine 3:1 (v/v)]. The absorption and steady-state fluorescence spectra were recorded using a Jasco v-670 spectrophotometer (Jasco, Japan) and a FluoroLog 3 spectrofluorimeter (Horiba Jobin Yvon, USA), respectively. The electrochemical experiments were conducted in N,N-dimethylformamide in the manner described in Ref. [34].

2.2. Synthesis

2.2.1. Synthesis of 6b,11-diazabenzo[a]fluorene-5,6-dione (1)

o-Aminopyridine (9.4 g, 0.05 mol) and 2,3-dichloronaphtho quinone (11.2 g, 0.05 mol) were refluxed in ethoxyethanol (100 ml) for 10 h. After cooling, the resulting dark brown precipitate was filtered and washed with ethanol to yield orange quinone (1) (7.73 g, 62%, m.p. 306 °C). The chemical structure of (1) was verified by ¹H NMR spectroscopy and CI mass spectrometry (Table 1).

Table 1 Product yield, m.p., R_{f_1} ¹H NMR and CI mass spectrometry data for compounds **1** and **2a**–**2d**.

Dye	Formula M.W.	m.p. ^a [°C]	$R_{\rm f}^{\rm b}$	Yield [%]	¹ H NMR ^c [CDCl ₃ , TMS (int), δ (ppm), J (Hz)]	CI MS m/z
1	C15H8N2O2 248.24	306, 302[27]	0.70	62	7.23 dt (1H, J ₁ = 1.0, J ₂ = 7.0), 7.50–7.56 m (1H), 7.62–7.75 m (2H),	249.0
2a	C ₂₁ H ₁₂ N ₄ 320.36	290, 285 [28]	0.73	75	7.82–7.86 m (1H), 8.13–8.22 m (2H), 9.34–9.31 m (1H) 7.19–7.22 m (1H), 7.57–7.63 m (1H), 7.77–7.90 m (4H), 7.99 d (1H, J = 7.5), 8.27–8.36 m (2H), 8.78 d (1H, J = 10.0), 9.39 dd (1H, J = 2.5, J_2 = 5.0)	321.1
2b	C ₂₃ H ₁₆ N ₄ 348.42	278	0.71	91	10.30 d (1H, $J = 7.5$ Hz) 2.39 s (3H), 2.43 s (3H), 7.04 dt (1H $J_1 = 1.0, J_2 = 7.0$), 7.45–7.52 m (1H), 7.60 s (1H), 7.67–7.83 m (2H), 7.93 d (2H, $J = 7.0$), 8.66 d (1H, $J = 7.5$),	349.1
2c	C ₂₁ H ₁₀ N ₄ Cl ₂ 389.25	305	0.83	63	9.16 dd (1H, J ₁ = 2.5, J ₂ = 10.0), 9.90–9.93 m (1H) 7.19 t (1H, J = 7.0), 7.59–7.66 m (1H), 7.67–7.76 m (1H), 7.82–7.88 m (1H), 7.99–8.03 m (1H), 8.25 s (1H), 8.32 s (1H), 8.70 d (1H, J = 7.0),	388.9
2d	C ₂₁ H ₁₀ N ₄ Br ₂ 478.16	350	0.82	70	9.13 d (1H, <i>J</i> = 7.5), 9.94 d (1H, <i>J</i> = 7.0) 7.32 t (1H, <i>J</i> = 7.5), 7.72–7.80 m (2H), 7.85–7.92 m (1H), 8.18–8.22 m (1H), 8.47 s (1H), 8.53 s (1H), 8.82 d (1H, <i>J</i> = 7.5), 9.10 d (1H, <i>J</i> = 7.5), 10.03 d (1H, <i>J</i> = 7.5)	478.8

^a Solvent: acetic acid.

^b Merck Silica Gel 60; eluent: toluene/pyridine 3:1 (v/v).

^c Abbreviations: d, doublet, dd, double doublet, t, triplet, dt, double triplet, and m, multiplet.

2.2.2. Synthesis of diazobenzo[a]fluorene (2a)

o-Phenylenediamine (1.5 g, 0.01 mol) and (1) (2.5 g, 0.01 mol) were refluxed in glacial acetic acid (28 ml) for 3.5 h. After cooling, the resulting dark yellow precipitate was filtered, washed with water, dried and recrystallized from acetic acid. The product was obtained with a 75% yield. The remaining dyes (**2b**–**2d**) were synthesized in the same manner from the appropriate *o*-phenylenediamine. The chemical structure of dyes (**2b**–**2d**) was verified by ¹H NMR spectroscopy and CI mass[spectrometry (Table 1).

2.3. Quantum chemical calculations

The geometries of all of the dyes, radical cations and radical anions were calculated using the B3LYP density functional theory method [35,36] in the Gaussian 03 suite of programs [37]. The calculations were conducted for the ground state (E_{GS}) using the standard 6-31 G^* basis set.

2.4. Photochemical experiments

In all of the photochemical experiments, a xenon lamp (Optel ZX 500 W, Poland) and Rayonet Reactor RPR 200 (Southern New England Ultraviolet Co, USA) equipped with eight lamps emitting light at 419 nm were used as a light source for dyes (**2a**–**2d**) and (**1**), respectively. The specific wavelength of xenon lamp was isolated using a band pass light filter (450 ± 10 nm). The light intensity of xenon lamp and Rayonet Reactor was measured using the potassium ferrioxalate [K₃Fe(C₂O₄)₃ × 3H₂O] actinometric method [38] and uranyl oxalate actinometry [39], respectively. Free radical polymerization was conducted in a solution composed of 1 ml of 1-methyl-2-pyrrolidone and 4 ml of **TMPTA**. The dye concentration was maintained at 0.1 mM for (**1**) and (**2a**–**2c**) and 0.017 mM for (**2d**). The concentration of the electron donors/acceptors was 10 mM. The fluorescence quantum yield of the dye (Φ_{fl}) was calculated from Eq. (1)

$$\Phi_{\rm fl} = \Phi_{\rm ST} \left(\frac{{\rm Grad}_X}{{\rm Grad}_{\rm ST}} \right) \times \left(\frac{\eta_X^2}{\eta_{\rm ST}^2} \right) \tag{1}$$

where Φ_{ST} and Φ_X denote the fluorescence quantum yield of the Rhodamine 101 standard ($\Phi_{ST} = 1.00$ in ethanol + 0.01% HCl [40]) and the tested dye, respectively. Grad_{ST} and Grad_X are the gradients obtained from the plot of the integrated fluorescence intensity as a function of the absorbance of the standard and tested dye, respectively, at their excitation wavelengths. η_{ST} and η_X are the

refractive indices of the standard and tested dye solvent, respectively.

The rate of polymerization (R_p) and double bond conversion (p) was calculated using Eqs. (2) and (3),

$$R_{\rm p} = \frac{\frac{Q}{s} \times M}{n \times \Delta H_{\rm p} \times m}$$
(2)

$$p = \left(\frac{\Delta H_{\rm t}}{n \times \Delta H_{\rm p}}\right) \times 100\% \tag{3}$$

where Q/s is heat flow per second during the reaction, m is the mass of the monomer in the sample, M is the molar mass of the monomer, n is the number of double bonds per monomer molecule, ΔH_t is the heat generated during irradiation and ΔH_p is the theoretical enthalpy for the complete conversion of acrylate double bonds [41]. A PT 401 temperature sensor (Elmetron, Poland) was immersed in the sample to detect the heat flow. The measurements were



Scheme 2. Synthesis of dyes 1 and 2a–2d (i) ethoxyethanol, reflux 10 h, and (ii) glacial acetic acid, 3.5 h.

Table 2

Spectroscopic parameters λ [nm], ε (M⁻¹ cm⁻¹), Stokes shift [nm] and fluorescence quantum yield (Φ_{fl}) for compounds 1 and 2a–2d.

Dye	$\lambda_{\max}^{a}(\varepsilon)$	$\lambda_{\max}^{\mathbf{b}}(\varepsilon)$	$\lambda_{\max}^{c}(\varepsilon)$	$\lambda_{\max}^{d}(\varepsilon)$	λ_{em}^{a}	$\lambda_{em}{}^{b}$	λ _{em} c	λ_{em}^{d}	Stokes shift ^a	Stokes shift ^b	Stokes shift ^c	Stokes shift ^d	$\Phi_{\mathrm{fl}}{}^{\mathrm{a}}$	$\Phi_{\mathrm{fl}}{}^{\mathrm{b}}$	$\Phi_{\rm fl}{}^{\rm c}$	$\Phi_{\mathrm{fl}}{}^{\mathrm{d}}$
1	399 (2300)	400 (7800)	393 (6300)	389 (5800)	_	_	_	_	_	_	_	_	_	_	_	_
2a	423 (sh),	427 (sh),	428 (sh),	428 (sh),	482	504	484	485	39	58	36	39	0.14	0.62	0.13	0.12
	443 (9800)	446 (9900)	448 (12,700)	446 (13,100)												
2b	423 (sh),	425 (sh),	426 (sh),	425 (sh),	479	495	478	481	36	49	31	35	0.20	0.66	0.19	0.16
	443 (11,100)	446(9700)	447 (12,000)	446 (14,100)												
2c	440 (sh),	441 (sh),	443 (sh),	441 (sh),	495	534	512	512	35	73	47	50	0.13	0.51	0.14	0.15
	460 (10,700)	461 (12,400)	465 (14,300)	462 (11,700)												
2d	440 (sh),	443 (sh),	445 (sh),	445 (sh),	497	517	512	514	35	54	45	50	0.13	0.23	0.15	0.14
	462 (8300)	463 (13,000)	467 (13,400)	464 (15,000)												

^a Chloroform.

^b 1-Methyl-2-pyrrolidone.

^c Cyclohexene oxide.

^d Tetrahydrofuran.

performed at ambient temperature, and the polymerizing mixture was not deaerated before curing.

3. Results and discussion

3.1. Synthesis, spectroscopic and electrochemical characterization and quantum chemical calculations of compounds (1) and (2a–2d)

Compounds (1) and (2a-2d) were prepared in a one- or twostage synthesis, as outlined in Scheme 2. In the first step, *o*-aminopyridine was cyclized with 2,3-dichloro-1,4-naphthoquinone in boiling ethoxyethanol yielding (1), which was then refluxed in glacial acetic acid with the appropriate *o*-phenylenediamines to produce (2a-2d). The crude dyes (2a-2d) were purified by recrystallization from acetic acid until a constant molar excitation coefficient and TLC purity were obtained. The dyes were obtained in good yields (62–91%). The melting points of the synthesized dyes were measured and compared with the literature data for compounds (1) [27] and (2a) [28] (Table 1).

The chemical structure of the dyes was verified by ¹H NMR spectroscopy and CI mass spectrometry (Table 1).

The ¹H NMR spectrum of (**1**) in CDCl₃ shows eight aromatic protons characterized by 5 one- or two-proton multiplets and one double triplet appearing at δ = 7.23 (J_1 = 1.0, J_2 = 7.0 Hz). The ¹H NMR spectra of the diazobenzo[a]fluorene derivatives (**2a**–**2d**) are similar, and the aromatic protons are spread over the region



Fig. 1. Normalized absorption (A) and emission (B) spectra of dye 2b in 1-methyl-2-pyrrolidone (dye concentration: 0.01 μM).

7.04–10.30, except for the aliphatic CH₃ group singlets in the (**2b**) ring system centered at $\delta = 2.39$ and $\delta = 2.43$. As shown in Table 1, the chemical shifts, multiplicity and integration of the relevant groups of protons in the ¹H NMR data are consistent with the dye structures. For compounds (**1**) and (**2a**–**2d**) protonated molecules $[M + H]^+$ or $[M]^+$ are usually produced, confirming their molecular weight and chemical structure.

Table 2 summarizes the spectroscopic properties (UV–Vis absorption and fluorescence) of the precursor (1) and the dyes (2a-2d) in chloroform, 1-methyl-2-pyrrolidone, cyclohexene oxide and tetrahydrofuran. In addition, absorption and fluorescence spectra of dye (2b) are presented in Fig. 1.

The intermediate of compound (1) exhibits weak absorption in the UV spectrum close to the visible range (Table 2). It is evident that the incorporation of a quinoxaline moiety into (1) greatly influences the spectroscopic properties of (**2a**–**2d**), because the conjugated system in the molecule is more planar and rigid. The solvent polarity has little influence on the spectroscopic properties.

The derivatives (**2a**–**2d**) exhibit one broad absorption band (with a shoulder) in the visible region located at 423–467 nm. The position of the visible absorption band depends on the character of the substituents (R). Incorporation of two electrondonating substituents (CH₃) in (**2b**) does not influence the absorption spectrum compared to the unmethylated dye in different solvents. The presence of electron-withdrawing halogens (Cl, Br) in the structures of dyes (**2c**) and (**2d**) causes a red shift of their λ_{max} due to p– π conjugation of these substituents with aromatic system.

The results in Table 2 illustrate that all of the tested dyes (2a-2d) exhibit fluorescence with an emission band characterized by a Stokes shift of ≈ 31 to 73 nm. In addition, the absorption and emission spectra are nearly mirror images of each other with

Table 3		
Electrochemical ^a and guantum chemical	calculations results	for dyes 1 and 2a-2d

Dye	Oxida proce	ation ess	Reduct	ion proo	Quantum chemical calculations				
	E _{ox} [V]	$E_{\text{ox}/2}$ [V]	E ^I red [V]	E ^{II} red [V]	ΔE^{I}_{p} [V]	$\begin{bmatrix} I_{p} & E_{red/2}^{I} & E_{red}^{II} \\ I & [V] & [V] \end{bmatrix}$		IP _s [kJ mol ⁻¹]	EA _s [kJ mol ⁻¹]
1	b	-	-0.84	-1.36	0.093	-0.81	-1.30	764.46	-160.97
2a	1.22	1.17	-1.21	-1.56	0.085	-1.10	-1.50	654.34	-78.18
2b	1.23	1.16	-1.23	-1.61	0.073	-1.17	-1.54	642.78	-70.46
2c	1.29	1.22	-1.13	-1.31	0.083	-1.08	-1.27	670.82	-120.86
2d	1.34	1.28	-1.11	-1.28	0.076	-1.08	-	667.97	-121.91

^a Data obtained at a scan rate of 10 mV s⁻¹.

^b Very weak peak.



Fig. 2. Cyclic voltammograms of dyes 2c (A – oxidation) and 2b (B – reduction) in N,N-dimethylformamide. Scan rate: 10 mV s⁻¹.



Scheme 3. Free radical polymerization in the presence of electron donors.

overlapping bands corresponding to the $0 \rightarrow 0$ transition. The fluorescence of halogen-substituted dyes (**2c**) and (**2d**) is red shifted in comparison with the unsubstituted analog, while the methyl-substituted derivative (**2b**) exhibits a blue shift. The fluorescence quantum yield of the dyes (**2a**–**2d**) is presented in Table 2. The dyes (**2a**–**2d**) exhibit fluorescence quantum yields ($\Phi_{\rm fl}$) in the range of 0.12–0.66 depending on the solvent and chemical structure of the dye. Dye (**2d**) exhibits the lowest $\Phi_{\rm fl}$ due to presence of Br (heavy atom), which promotes intersystem crossing and stabilizes the molecule's triplet state [29–31].

It is well known [42] that cyclic voltammetry is a good analytical method for characterizing the electrochemical properties of dyes. The electrochemical data are presented in Table 3, and the cyclic voltammograms of dyes (**2b**) and (**2c**) are presented in Fig. 2.

In all of the cases, the electrochemical reduction is a two-step process. The first step is irreversible, and the second step is reversible. Oxidation of the tested dyes is a quasi-reversible process ($\Delta E_p^l = 0.06-0.1$ V). The location of the oxidation and reduction peaks depends on the dye structure. The obtained results clearly indicate that dyes (**2a**) and (**2b**) are more readily oxidized than the halogen-substituted analogs (**2c**) and (**2d**), which is illustrated by the position of the oxidation peak at 1.22 V and 1.23 V for dyes (**2a**) and (**2b**), respectively, and at 1.29 V and 1.34 V for dyes (**2c**) and (**2d**), reduced at lower potentials (-1.13 V and -1.11 V, respectively) than all of the other compounds. These observations are in good agreement with the electronic effects of CH₃ (+I, +M) and halogen (-I, +M) substituents.

Quantum chemical calculations of the electron affinity (EA_s) and ionization potential (IP_s) are shown in Table 3. The EA_s/IP_s were calculated as the difference in total energy for the neutral molecule in the ground state and the appropriate radical anion/radical cation in the ground state. The ionization potential and electron affinity of derivatives (2a-2d) are in good agreement with their involvement in oxidation/reduction processes and with the influence of the substituents on the behavior of the dye molecules.

3.2. Free radical polymerization

It is well known [19,20] that photoinduced electron transfer (PET) processes may involve two different types of dye sensitization. The first type is the photoreducible sensitization in which the dye is photoreduced in the presence of suitable reductants (Scheme 3), and the second type is the photooxidation of the dye by a strong electron acceptor (Scheme 4). Spectroscopic studies have revealed that compounds (1) and (2a–2d) could be employed as visible sensitizers for the collection of light \geq 400 nm.

To evaluate the ability of the dyes tested to initiate free radical polymerization, the values of the free energy change (ΔG^0_{el}) were calculated from the Rehm–Weller Eq. (4) [43]:

$$\Delta G_{\rm el}^0\left(\rm kJ\,mol^{-1}\right) = 97\left[E_{\rm ox}\left(\frac{D}{D^{*+}}\right) - E_{\rm red}\left(\frac{A^{*-}}{A}\right)\right] - \frac{Ze^2}{\varepsilon\alpha} - E_{00} \quad (4)$$

In this equation, $E_{\rm ox}(D/D^{\bullet+})$ and $E_{\rm red}(A^{\bullet-}/A)$ are the oxidation potential of the electron donor and reduction potential of the electron acceptor, respectively. In this calculation, the Coulombic energy $(Ze^2/\epsilon\alpha)$ was negligible with respect to the overall magnitude of the $\Delta G^0_{\rm el}$. The E_{00} is the excited singlet state energy of the dye (Table 4), which was calculated using Eq. (5):

$$E_{00} = \frac{hcN}{\lambda} \tag{5}$$

where *h* is Planck's constant, *c* is the speed of light in a vacuum $(3 \times 10^{17} \text{ nm s}^{-1})$, *N* is Avogadro's constant and λ is the wavelength



Scheme 4. Free radical polymerization in the presence of electron acceptors.

Table 4			
Thermodyna	amic properties of th	e tested photoredox p	airs. ^a
Dve	۸G.,b	٨Gu ^c	

Dye	ΔG _{el} ^b [kJ mol ⁻¹]	ΔG_{el}^{c} [kJ mol ⁻¹]	ΔG _{el} ^d [kJ mol ⁻¹]	$\Delta G_{\mathrm{el}}^{\mathrm{e}}$ [kJ mol ⁻¹]	$\Delta G_{\mathrm{el}}{}^{\mathrm{f}}$ [kJ mol $^{-1}$]	ΔG _{el} ^g [kJ mol ⁻¹]	E ₀₀ [kJ mol ⁻¹]
2a 2h	-34.80	-15.40	-75.04	-85.71	-89.78	-84.74	304.22
20 2c	-38.67 -22.60	-19.27 -3.20	-73.22	-83.89	-87.96	-82.80 -82.92	253.06 256.87
2d	-24.94	-5.54	-171.27	-181.94 157.46	-186.02	-180.97	240.84
1	—	—	-140.79	-137.40	-101.55	-150.49	246.04

^a For the calculation, the potential of the first electron acceptance was used.

^b With **A1** (*E*_{red}: -1.025 V) [43].

^c With **A2** (E_{red} : -1.225 V).

^d With **D1** (*E*_{ox}: 0.78 V).

^e With **D2** (*E*_{ox}: 0.67 V).

^f With **D3** (*E*_{ox}: 0.63 V).

^g With **D4** (E_{ox} : 0.68 V).

(nm) at the point where the normalized absorption and emission cross. The reduction and oxidation potentials of the electron donors/acceptors used were taken from the literature [44] or estimated in a separate experiment.

The results of the calculated thermodynamic parameters are listed in Table 4. The ΔG^0_{el} for the electron transfer process for all of the tested photoredox pairs is negative, which means that the PET for the bimolecular system studied is thermodynamically allowed and proceeds via the excited state of the dye.

Finally, the photoredox pairs consisting of a diazobenzo[a] fluorene dye and the appropriate coinitiators (**D1**–**D4** or **A1**, **A2**) were examined as initiators for the free radical polymerization of **TMPTA**. The efficiency of the polymerization initiated by the studied photoredox pairs was assessed from the heat flow during the irradiation. Figs. 3 and 4 show examples of the photopolymerization kinetic curves for the representative photoredox pairs. In addition, the rates of polymerization, inhibition time and efficiency of monomer conversion are shown in Table 5.

It is evident that compounds (1) and (2a–2d) initiate the polymerization process under both conditions (i.e. according to the reducible and oxidizable mechanism). The obtained data indicate that the efficiency of the polymerization strongly depends on the type of electron donor/acceptor and on the structure of the dye. It is apparent that dye (2d), which contains two bromine atoms, significantly accelerates the polymerization of TMPTA. Moreover, A2 is a more effective initiator than A1. As it



Fig. 3. Kinetics curves for TMPTA polymerization recorded for dyes 2a, 2b, 2c, and 2d and 1 in the presence of D3.



Fig. 4. Kinetics curves for TMPTA polymerization recorded for dye 2c in the presence of D1, D3, D4, and A2.

is well known from the literature [18] the rate of the photopolymerization depends on the efficiency of the excited state formation according to Eq. (6):

$$R_{\rm p} = k_{\rm p}[M] \left(\frac{I_{\rm a} \Phi_{\rm T} k_{\rm el}}{k_{\rm t}}\right)^{0.5} \tag{6}$$

in which I_a is the intensity of the absorbed light, Φ_T is the quantum yield of triplet state formation, k_p and k_t denote the rate constants of polymerization and chain termination steps, respectively, and k_{el} is the first order rate constant of the electron transfer. In dye (**2d**) the presence of two bromines [29–31] promotes intersystem crossing of the molecule stabilizing its triplet state (Φ_T). This fact is consistent with the lowest Φ_{fl} of this dye in 1-methyl-2-pyrrolidone (Table 2).

On the other hand, the optimum polymerization efficiency of **TMPTA**, which follows the reducible mechanism, was achieved for dye (**2b**) in the presence of **D3**, having the lowest E_{ox} .

Additionally, the free radical polymerization initiated by the tested photoredox pairs shows a significant inhibition time (Figs. 3 and 4). In general, the most efficient photoredox pair has the shortest inhibition time, which is related to the oxygen dissolved in the composition. The oxygen quenches both the triplet state of the dye and reacts with radical species generated by the dye/electron donor or acceptor systems. After the consumption of the oxygen, the initiating radicals react with the monomer.

fable 5
Rates of polymerization R_p [µmol s ⁻¹], inhibition times I_t [s] and percent conversions of the monomer [%].

Dye	A1			A2			D1			D2			D3			D4		
	R _p	%	Inhibition time, I _t	R _p	%	Inhibition time, I _t	R _p	%	Inhibition time, I _t	R _p	%	Inhibition time, I _t	R _p	%	Inhibition time, I _t	R _p	%	Inhibition time, I _t
2a	23.1	14	120	39.3	23	295	33.7	20	50	40.5	24	477	43.5	26	_	19.2	11	227
2b	19.6	12	25	44.6	26	222	58.5	19	37	31.0	18	490	40.5	24	-	23.3	14	267
2c	16.4	10	175	36.7	22	350	26.1	15	47	17.9	11	807	34.8	21	_	17.2	10	217
2d	24.1	14	150	73.4	43	375	32.8	19	135	1.1	<1	_	23.8	14	_	21.2	13	115
1	57.6	34	85	66.3	39	47	71.0	42	_	68.0	40	_	51.8	31	_	23.6	14	_

Dyes **2a**–**2d**: light (450 nm) intensity of 4.93×10^{17} [quant s⁻¹], dye **1**: light (419 nm) intensity of 1.6×10^{17} [quant s⁻¹].

4. Conclusions

Novel polyheterocyclic dyes based on a diazobenzo[a]fluorene system were successfully synthesized and characterized using ¹H NMR spectroscopy and CI mass spectrometry. The electrochemical properties of the examined dyes were characterized and found to be influenced by their chemical structure. The spectroscopic study of diazobenzo[a]fluorene dyes clearly indicates that the dyes tested are good candidates for potential application as a two-component photoinitiator system for multiacrylate free radical polymerization under visible light. Reducible sensitization is more efficient in comparison to oxidizable sensitization used with the application of the same group of dyes. The ability of each dye to act as a photoinitiator depends upon its chemical structure. Furthermore, the heavy atom present in the structure can promote the formation of the dye's excited triplet states facilitating electron transfer from these triplet states.

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