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Synthesis of novel oxidizable polymerization sensitizers based on the dithiinoquinoxaline skeleton

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1. Introduction

Industrial applications of photocuring are extremely varied and include metal coatings (automotive varnishes), the production of printed circuit boards and the generation of three-dimensional models [1]. Radical chain addition polymerization is one of the simplest and most widely used methods of polymer formation. In the industrial applications of this method, the polymerizable formulations are based on mono- and multifunctional (meth) acrylate, unsaturated polyester, and acrylated polyurethanes.

Many highly efficient UV initiators are commercially available [2]. These initiators differ in their mode of generation of reactive free radicals. During photolysis, type I initiators undergo a bond cleavage as shown in Scheme 1 for benzoin. Alternatively, the triplet state of type II initiators reacts with a H-donor compound such as tertiary amines, thiols, ethers and alcohols to yield the initiating radicals (Scheme 2).

At present, systems in which polymerization is sensitive to visible light are used in conjunction with visible emitting light sources, such as lasers and LEDs. These systems are of particular interest because of their use in many special applications, such as dental filing materials, photoresists, printing plates, highly pigmented coatings, holographic

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ABSTRACT

Novel dyes, based on the dithiinoquinoxaline skeleton, were synthesized and characterized using ¹H NMR spectroscopy and chemical ionization mass spectroscopy. Their spectral properties, such as absorption, emission spectra and quantum yield of fluorescence, were also measured. Electron donating properties of the title compounds were estimated on the basis of DFT calculations. The studied dyes were used as oxidizable sensitizers for 2,4,6-tris(trichloromethyl)-1,3,5-triazine (Tz). The dye/Tz photoredox pairs were found to be effective visible-wavelength initiators of free radical polymerization. The ability of these systems to act as photoinitiators strongly depended upon the free energy change of the photoinduced electron transfer from the excited dyes to Tz. It has been shown that the intermolecular electron transfer is the limiting step in the photopolymerization initiated by these studied initiator systems.

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recording and nanoscale micromechanics [2]. The most important component of such photopolymerized systems is the photoinitiators which should have efficient absorbance at long visible wavelengths.

One way to create a system in which polymerization can be photoinduced by visible light is to use a dye. In such dye based photoinitiator systems, the initiating radicals are typically generated by a photoinduced electron transfer. These systems involve a second component, an appropriate co-initiator, that participates in the electron transfer process. Many attempts have been made to develop such two component systems [3–12]. Depending on the nature of the dye involved, two distinct sensitizations need to be considered: the electron transfer from the co-initiator to the excited, photoreducible dye [3–7] and the electron transfer from the excited, photo-oxidizable dye to the co-initiator (Scheme 3) [8–12]. Then the initiating radicals are formed from cleavage of the oxidized or reduced form of the co-initiator.

In photo-oxidizable sensitization, the commonly used coinitiators are N-alkoxypyridinium salts and the derivatives of 2,4,6-tris(trichloromethyl)-1,3,5-triazine. These compounds yield alkoxy radicals [8-12] and halogenmethyl radicals [6,7] which initiate polymerization. However, not all dyes are able to initiate photopolymerization with the aid of Tz [7].

As mentioned above, in oxidizable sensitization dyes undergo the photooxidation and they should have a low ionization potential. It is well known that 1,4-dithiin and its dibenzo-homolog, thianthrene, are characterized by a notably low first oxidation potential



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Scheme 1. Type I initiator.

due to the π -donor ability of the sulfur atom [13]. The thianthrene radical cation is readily formed through oxidation either homogeneously in solution [14–16] or electrochemically [17]. Moreover, polyheterocyclic systems with fused 1,4-dithiine units are electron donors with moderate oxidation potentials [18]. Therefore, the main goals of this study were to synthesize sensitizers based on the dithiinoquinoxaline skeleton (Scheme 4) and to evaluate these dyes' spectroscopic, photophysical, and electron donating properties. This paper also reports the application of these dyes as visible-light sensitizers for 2,4,6-tris(trichloromethyl)-1,3,5-triazine (**Tz**). Finally, experiments demonstrated that these new photo-oxidizable sensitization systems could be used as visible-light photo-initiators for the free radical polymerization of acrylate monomers.

2. Experimental

2.1. General

Trimethylolpropane triacrylate (TMPTA), 1-methyl-2-pyrrolidone (MP) and the necessary synthesis reagents were purchased from Sigma–Aldrich (Poznan, Poland). **Tz** was purchased from Wako-Chemicals. The dyes **4a–4b** and **6a–6f** were identified and characterized via ¹H NMR spectroscopy [Bruker Avance DPX 250, CDCl₃, drop of CF₃COOH, TMS internal standard, δ (ppm)]. Their purity was confirmed using TLC [Merck Silica gel 60, solvent: 3:1 (v/v) toluene/pyridine]. The chemical ionization mass spectra were recorded on a Finnigan MAT 94 spectrometer with isobutane application. Absorption and steady-state fluorescence spectra were recorded using a Jasco V-670 spectrophotometer (Jasco, Japan) and a Lumina fluorescence spectrometer (Thermo Scientific, USA), respectively.

2.2. Synthesis

2.2.1. Synthesis of 6,7-dimethyl-2,3-diisothiouronium quinoxaline dihydrochloride **2b** [19]

6,7-Dimethyl-2,3-dichloroquinoxaline (4.7 g, 0.021 mol) and thiourea (3.48 g 0.046 mol) were refluxed in ethanol (55 ml, 96%) for 5 h. After cooling, the resulting goldish-orange precipitate was filtered and washed with 5 ml of ethanol to yield **2b** (4.59 g, 58%). **2b** was used in the next step of the synthesis without purification. The **2a** diisothiouronium quinoxaline dihydrochloride was synthesized, in a similar fashion, from 2,3-dichloroquinoxaline starting material.

2.2.2. Synthesis of 6,7-dimethylquinoxaline-2,3-dithiol **3b** [19]

6,7-dimethyl-2,3-diisothiouronium quinoxaline dihydrochloride **2b** (6.495 g, 0.0036 mol) was suspended in water (24 ml) and a solution of KOH (3.2 g, 0.09 mol) in water (13 ml) was added. The resulting orange precipitate was filtered, washed with water and



Scheme 2. Type II initiator.

suspended in water (10 ml). To this suspension a saturated aqueous KOH solution was added until the precipitate was completely dissolved. Then 1 M hydrochloric acid was added with stirring to adjust the pH of the solution to pH \approx 1. The resulting dark-brown precipitate was filtered, washed with water and dried to yield **3b** (3.502 g,

itate was filtered, washed with water and dried to yield **3b** (3.502 g, 92%). The **3a** quinoxaline-2,3-dithiol was synthesized, in a similar fashion, from 2,3-dichloroquinoxaline starting material. **3b** was used in to the next step of the synthesis without purification.

2.2.3. Synthesis of [1,4]dithiino[2,3-b:5,6-b']diquinoxaline 4a

2,3-Dichloroquinoxaline **1a** (0.995 g, 0.005 mol), quinoxaline-2,3-dithiol **3a** (0.971 g, 0.005 mol) and triethylamine (1 ml) were refluxed in dimethylformamide (15 ml) for 5 h. After cooling, the resulting precipitate was filtered, washed with water and ethanol to yield **4a** (1.202 g, 75%, m.p. > 360 °C).

2.2.4. Synthesis of 3-chloropyrido[2",3":5,6]pyrazino[2',3':5,6] [1,4]dithiino[2,3-b]quinoxaline **6b**

2,3,7-Trichloropyridipyrazine **5b** (1.172 g, 0.005 mol), quinoxaline-2,3-dithiol **3a** (0.971 g, 0.005 mol) and triethylamine (1 ml) were refluxed in dimethylformamide (30 ml) for 5 h. After cooling, the resulting precipitate was filtered, washed with water and ethanol, dried and recrystallized from chloroform. The product **6b** (1.415 g, m.p. 339–341 °C) was obtained with an 80% yield. The other dyes were synthesized in the same manner from the appropriate dichloropyridopyrazines **5** and quinoxaline-2,3-dithiols **3**. Table 1 presents the yield, melting point, elemental analysis, ¹H NMR and CI MS data for these dyes.

2.3. Photochemical experiments

All photochemical experiments were carried out in a Rayonet Reactor RPR 200 (Southern New England Ultraviolet Co, USA) equipped with eight lamps emitting light at 419 nm. The illumination intensity was measured using uranyl oxalate actinometry [21].

The fluorescence quantum yield of the dye (Φ_{DYE}) was calculated from the following equation:

$$\Phi_{\text{DYE}} = \Phi_{\text{ST}} \frac{G_{\text{DYE}} \cdot \eta_{\text{DYE}}^2}{G_{\text{ST}} \cdot \eta_{\text{ST}}^2} \tag{1}$$

where the subscripts ST and DYE denote standard and test respectively, Φ is the fluorescence quantum yield, *G* is the gradient from the plot of integrated fluorescence intensity versus absorbance, and η is the refractive index of the solvent. Rhodamine 101 in ethanol was used as the standard ($\Phi_{\text{ST}} = 1.0$ [22]).

In all the polymerization experiments, a cut-off filter was used to eliminate wavelengths shorter than 400 nm. Free radical photopolymerization reactions were conducted in a solvent mixture of 1 ml of MP and 4 ml of TMPTA. The concentration of dye and **Tz** were maintained at 50 μ M and 1 mM, respectively. The solutions were irradiated for 180 s. The rate of polymerization (R_p) was calculated from Eq. (2):

$$R_{\rm p} = Q_{\rm s} \cdot M / n \cdot \Delta H_{\rm p} \cdot m \tag{2}$$

In this expression, 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, and ΔH_p is the theoretical enthalpy for complete polymerization of acrylate double bonds (20.6 kcal/mol) [23]. The heat flow was measured with a PT 401 temperature sensor (Elmetron, Poland), immersed in the sample. A polymerizing mixture containing the dye without a co-initiator was used as a reference sample.



Scheme 3. Photo-oxidizable sensitization.

2.4. Quantum chemical calculations

The geometries of all species were optimized by the B3LYP density functional method [24,25] as implemented in the Gaussian 03 suite of programs [26]. The optimized structures were characterized by harmonic frequency analysis as local minima (all frequencies real). These calculations were performed for the ground states using a standard 6-31G(d) basis set. The gas-phase vertical ionization potentials (IPV_{gas}) were calculated from the differences in total energy between the neutral molecule and its radical cation at the optimized geometry of the neutral molecule. Relative energies were obtained only by single point calculations at the B3LYP/6-31+G(d) level on optimized structures of the ground states and of cation radicals in neutral geometry. The adiabatic ionization potentials (IPgas) were obtained in the same way, but using the total energy obtained from the optimized geometry of the radical cation. Bulk solvent effects were studied by performing selfconsistent reaction field (SCRF) calculation by using the PCM



	R	Х	Y
4a	Н	СН	Н
4b	CH_3	СН	Н
6a	Н	N	Н
6b	Н	N	Cl
6c	Н	N	Br
6d	CH_3	N	Н
6e	CH_3	N	Cl
6f	CH_3	N	Br
1			

Scheme 4. Structure of the studied dyes.

method on the gas-phase optimized geometry of the neutral molecule and its radical cation. The dielectric constant of acetonitrile ($\varepsilon = 36.64$) was used throughout. In MeCN the ionization potentials IP_{MeCN} were calculated by subtracting the total energies of the neutral molecule and radical cation obtained from single point IEFPCM calculation.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization of dyes

The basis of the design of the studied dyes was literature reports that concerned the formation of a thianthrene radical cation [14–17]. Due to continuing interest in the applications of oxidizable sensitizers, we prepared dyes based on the dithiinoquinoxaline skeleton (**4**, **6**). To the best of our knowledge, derivatives **6** are so far not known.

Compounds **4** and **6**, with fused 1,4-dithiine units, were synthesized by a three stage synthesis shown in Scheme 5. Our route to dyes **4** starts with 2,3-dichloroquinoxalines (**1a**, **1b**), which react with thiourea in refluxing ethanol (96%) to give the corresponding derivatives of 2,3-diisothiouronium quinoxaline dihydrochloride (**2a**, **2b**) in 60% yield [19]. In the next step, quinoxalines-2,3-dithiols (**3a**, **3b**) are obtained by subsequent treatment of **2** with KOH and HCI [19]. Finally, the desired dyes (**4a** and **4b**) were synthesized by refluxing **3a** or **3b** with 2,3-dichloroquinoxaline (**1a**) in dimethylformamide with triethylamine. Dyes **6** were synthesized in the same manner starting from the appropriate 2,3-dichloropyridopirazines (**5a**–**5c**), which were obtained according to procedure described in Ref. [11].

The crude dyes were purified by recrystallization from chloroform until a constant molar extinction coefficient and TLC purity were obtained. Dyes **4** and **6** were synthesized in excellent yield (69–80%), and their chemical structures were verified by ¹H NMR and CI mass spectra (Table 1). The spectroscopic properties (absorption and fluorescence) of dyes **4** and **6** are presented in Table 2.

Dyes **4** and **6** have absorption bands located at approximately 390 nm, and emission bands located at approximately 480 nm characterized by a $\sim 64-98$ nm Stokes shift. These values indicate that the geometry of the singlet excited state does not differ greatly from the geometry of the ground state. The electronic absorption (UV–vis) and emission spectra of dye **6f** are presented in Fig. 1. The spectra of the other dyes are presented in Figs. 1S–7S (Supplementary data). For all dyes tested, the absorption and fluorescence

Table 1
Melting point, yield, elemental analysis, ¹ H NMR and CI mass spectra of dyes 4 and 6

Dye	M.p.	Yield	Elemental analysis	MS CI	¹ H NMR
-	[°C]	[%]	-	m/z	J [Hz]; δ [ppm]
4a	>360 350 [20]	75	Anal. Calcd for C ₁₆ H ₈ N ₄ S ₂ C, 59.98; H, 2.52; N, 17.49; S, 20.02 Found: C, 59.4; H, 2.5; N, 17.6; S, 19.9	M = 320.4 320.1 [M] ⁺ 321.1 [M+H] ⁺ , 322.1 [M+2H] ⁺	7.93–7.97 (m, 4H), 8.16–8.20 (m, 4H)
4b	>360	76	Anal. Calcd for C ₁₈ H ₁₂ N ₄ S ₂ C, 62.05; H, 3.47; N, 16.08; S, 18.40 Found: C, 62.0; H, 3.4, N, 16.1; S, 18.3	M = 348.45 348.1 [M] ⁺	2.61 (s, 6H), 7.94–7.96 (m, 2H), 8.62 (s, 2H), 9.24 (s, 2H)
6a	>360	41	Anal. Calcd for C ₁₅ H ₇ N ₅ S ₂ C, 56.06; H, 2.20; N, 21.79; S, 19.95 Found: C, 56.1; H, 2.1, N, 21.7; S, 20.0	M = 321.38 321.1 [M] ⁺	7.80–7.89 (m, 4H), 7.98–8.10 (m, 3H)
6b	339–342	80	Anal. Calcd for C ₁₅ H ₆ N ₅ S ₂ Cl C, 50.63; H, 1.70; N, 19.68; S, 18.02 Found: C, 50.7; H, 1.6, N, 20.0; S, 17.9	M = 355.83 355.9 [M] ⁺	7.85–7.97 (m, 2H), 8.04–8.11 (m, 3H), 9.13 (s, 1H)
6c	>360	79	Anal. Calcd for C ₁₅ H ₆ N ₅ S ₂ Br C, 45.01; H, 1.51; N, 17.50; S, 16.02 Found: C, 44.8; H, 1.5, N, 17.6; S, 16.1	$\begin{array}{l} M = 400.28 \\ 399.9 \ [M]^+ , 400.9 \ [M{+}H]^+ , \end{array}$	7.84–7.91 (m, 2H), 8.01–8.09 (m, 3H), 9.18 (s, 1H)
6d	>360	39	Anal. Calcd for C ₁₇ H ₁₁ N ₅ S ₂ C, 58.43; H, 3.17; N, 20.04; S, 18.35 Found: C, 58.5; H, 3.2, N, 20.1; S, 18.3	M = 349.44 349.1 [M] ⁺	2.63 (s, 6H), 7.05–7.13 (m, 3H), 7.91 (s, 2H)
6e	>360	72	Anal. Calcd for C ₁₇ H ₁₀ N ₅ S ₂ Cl C, 53.19; H, 2.63; N, 18.24; S, 16.71 Found: C, 53.3; H, 2.7, N, 18.1; S, 16.5	$\begin{split} M &= 383.88 \\ 384.1 \ [M]^+ \\ 386.1 \ [M+2H]^+ \end{split}$	2.52 (s, 6H), 7.76–7.83 (m, 3H), 8.56–8.57 (m, 1H)
6f	330–332	80	Anal. Calcd for C ₁₇ H ₁₀ N ₅ S ₂ Br C, 47.67; H, 2.35; N, 16.35; S, 14.97 Found: C, 47.7; H, 2.4, N, 16.4; S, 15.0	$\begin{array}{l} M = 428.33 \\ 428.1 \ [M]^+, 430.0 \ [M+2H]^+ \end{array}$	2.63 (s, 6H), 7.05–7.09 (m, 3H), 7.91–7.96 (m, 1H)

spectra were nearly mirror images of each other, with overlapping bands corresponding to the $0 \rightarrow 0$ transition.

It is evident that the presence of additional nitrogen in dyes **6a** and **6d** caused a small hypsochromic effect (6–7 nm) in comparison to dyes **4a** and **4b**, respectively. The position of the absorption band

depended on the character of a dye's halogen group. For dyes **6a** and **6d**, the absorption bands were located at 380 nm and 395 nm, respectively. The presence of a chlorine substituent in dyes **6b** and **6e** caused a red-shift in the absorption band compared to the corresponding unchlorinated dye. A larger bathochromic effect was



Scheme 5. i) Thiourea, 96% EtOH; ii) KOH, HCl; iii) DMF, Et₃N.

 Table 2

 Spectroscopic and photophysical parameters of the examined dyes

_									
	Dye	λ _{max} a [nm]	$\varepsilon^{a} [dm^{3} mol^{-1} cm^{-1}]$	λ _{max} b [nm]	$\varepsilon^{b} [dm^{3} mol^{-1} cm^{-1}]$	λ _{fl} a [nm]	$\Phi_{\mathrm{fl}}{}^{\mathrm{a}}$	Stokes shift [nm]	E ^{00a} [kJ mol ⁻¹]
	4a	386	20,100	389	24,000	456	0.073	70	280.0
	4b	388	19,800	391	31,600	466	0.070	74	278.0
	6a	380	20,400	389	22,300	455	0.065	75	278.4
	6b	400	24,000	404	28,800	484	0.054	84	265.3
	6c	403	22,200	406	21,200	486	0.050	90	278.0
	6d	395	17,200	393	17,000	459	0.067	75	275.7
	6e	402	17,000	400	18,900	500	0.060	98	264.3
	6f	406	26 400	404	22 300	502	0.053	96	260.1

^a In 1-methyl-2-pyrrolidone.

^b In THF.



Fig. 1. Normalized absorption (black) and emission (gray) spectra of dye $6f\ (3\ \mu\text{M})$ in MP.

observed for dyes **6c** and **6f**. In these dyes, the absorption bands were located at approximately 403 nm. Additionally, the presence of two methyl substituents had a small bathochromic effect (3-12 nm) on the position of these molecules' absorption bands.

The fluorescence quantum yields ($\Phi_{\rm fl}$) of the studied dyes are presented in Table 2. These dyes have a low value of $\Phi_{\rm fl}$, which

ranges from 0.050 to 0.073. As can be seen from these data, adding heavy atoms such as Br to the studied fluorescent system caused a decrease of $\Phi_{\rm fl}$. The molecule's triplet state stabilization results in increased efficiency of the intersystem crossing process that causes this effect.

3.2. Sensitized free radical photopolymerization

The spectroscopic studies revealed that the dyes **4** and **6** have an absorption bands around 400 nm and could be applied as visible sensitizers for the collection of light >400 nm. The well known mechanism of the dye-sensitized photodecomposition of **Tz** [6] is presented in Scheme 3. Irradiation of these two component systems leads to electron transfer from the excited sensitizer (Dye^{*}) to the **Tz**. The initiating halogenmethyl radicals are formed from cleavage of the radical anion of **Tz**. The electron transfer from the excited dyes to the **Tz** is thermodynamically allowed if the free energy (ΔG_{et}), calculated from the Rehm–Weller equation (Eq. (3)) [27], is negative.

$$\Delta G_{\rm et}(kJ \, {\rm mol}^{-1}) = 97[E_{\rm ox}(S/S^{+}) - E_{\rm red}(A^{-}/A)] - E^{00}(S) - Z_1 Z_2 / \epsilon r_{12}$$
(3)

In this equation (Eq. (3)), E_{ox} (S/S⁺⁺) and E_{red} (A⁺⁻/A) are the oxidation potential of the dye and the reduction potential of the **Tz**, respectively. The term E^{00} (S) is the singlet excited state energy of the dye. The last term represents the Coulombic energy necessary to form an ion pair with charges Z_1 and Z_2 in a medium of dielectric constant ε for a distance r_{12} . This factor can very often be ignored taking into account the overall value of ΔG_{et} .

In order to be able to calculate ΔG_{et} , the oxidation potentials (E_{ox}) of the studied dyes **4** and **6** should be measured. Unfortunately, in solvents which are commonly used in electrochemical experiments (CH₃CN, DMF) the solubility of the studied dyes is too low. Therefore, the oxidation potentials of these compounds were estimated on the basis of DFT calculations. There are several ways to estimate the oxidation potentials. The first, and the simplest one, involves the calculation of the energy of highest occupied molecular orbital (E_{HOMO}) of a neutral compound. The second way to obtain the oxidation potentials involves the calculation of ionization potentials in the gas-phase or in the solvent. In order to select the suitable way to estimate the E_{HOMO} , IPV_{gas}, IP_{gas} and IP_{MeCN} of



Scheme 6. Dibenzodioxin (7), thianthrene (8), phenoxathiine (9), 2,3,7,8-tetramethoxythianthrene (10), 2,3,7,8-tetramethoxyphenoxathiine (11), 2,3;7,8-bis(ethylenedioxy) thianthrene (12), 2,3;7,8-bis(ethylenedioxy)phenoxathiine (13).

Table 3

Energy of the HOMO orbitals (eV), ionization potentials (eV) for compounds 7-13 and their experimental oxidation potentials (V).

	$E_{1/2}^{\text{ox}}$	$-E_{HOMO}$	IPV_{gas}	IPgas	IP _{MeCN}
7	1.394 ^a	0.19620	7.35	7.00	5.24
8	1.234 ^a	0.20950	7.57	6.97	5.29
9	1.201 ^a	0.20105	7.41	6.88	5.17
10	1.01 ^b	0.19141	6.90	6.31	5.00
11	0.92^{b}	0.18297	6.73	6.13	4.80
12	0.86^{b}	0.19382	6.97	6.25	5.06
13	0.77 ^b	0.18474	6.78	6.07	4.85
		R = 0.705	0.853	0.955	0.846

^a In CH₃CN calculated as $E_{1/2}^{ox}(vs SCE) = E_{1/2}^{ox}(vs Fc/Fc^+) + 0.40; E_{1/2}^{ox}(vs Fc/Fc^+)$ from Ref. [28].

^b In CH₃CN versus SCE from Ref. [29].

structurally related compounds (Scheme 6) for which redox potentials are available in the literature [28,29].

Table 3 compiles the calculated E_{HOMO} , IPV_{gas}, IP_{gas} and IP_{MeCN} for these selected compounds together with the experimentally determined reversible redox potentials ($E_{1/2}^{\text{ox}}$). The best linear correlation (r = 0.95) was found between the IP_{gas} and $E_{1/2}^{\text{ox}}$ (Fig. 2). This relationship are given by Eq. (4)

$$E_{1/2}^{\text{ox}} = (-2.35 \pm 0.47) + (0.52 \pm 0.07) \text{IP}_{\text{gas}}$$
(4)

where $E_{1/2}^{\text{ox}}$ is the reversible oxidation potential versus SCE and IP_{gas} is the adiabatic ionization potentials. The Eq. (4) made it possible to estimate the E_{ox} of dyes **4** and **6**. These data are presented in Table 4. The results indicate that dyes with two methyl groups (**4b**, **6d**–**6f**) are more readily oxidized than unsubstituted dyes (**4a**, **6a**–**6c**).

Once the E_{ox} of dyes **4** and **6** had been estimated, the ΔG_{et} could be calculated using the $E^{00}(S)$ of the studied dyes (see Table 2) and the reduction potential of **Tz** (-0.97 in CH₃CN versus SCE [7]). The calculated thermodynamic parameters listed, in Table 4, indicated that all the tested dye/**Tz** systems posses a favorable thermodynamic driving force upon exposure to light ($-\Delta G_{et} > 15 \text{ kJ mol}^{-1}$). This means that the excited-state photoelectron transfer is quite facile.

Finally, the dye/Tz systems were examined for potential applications as initiators for the free radical polymerization of the Table 4

Estimated oxidation potential ($E_{1/2}^{\text{ox}}$, V), thermodynamic data (ΔG_{et} , kJ mol⁻¹), rate of photopolymerization (R_{p} , μ mol s⁻¹) and inhibition time (t_{inh} , s).

Dye	$E_{1/2}^{\mathrm{ox}}$	$\Delta G_{\rm et}^{\ a}$	R _p	t _{inh}
4a	1.48	-42.3	38.2	28
4b	1.37	-51.0	19.1	57
6a	1.57	-32.0	32.0	35
6b	1.61	-15.0	26.5	54
6c	1.60	-28.7	53.7	25
6d	1.45	-41.0	27.2	42
6e	1.50	-24.7	31.6	37
6f	1.49	-21.5	24.3	53

^a **Tz** $E_{\text{red}} = -0.97$ in CH₃CN versus SCE from Ref. [7].

trimethylolpropane triacrylate monomer. From a practical point of view, the most important property of the initiator system is the ability to initiate the photopolymerization of monomers in an air atmosphere. Therefore, in our investigation, the efficiency of the polymerization initiated by the studied photoredox systems was measured in an air equilibrium composition. The polymerization rate of TMPTA was measured indirectly from the reaction's heat flow during irradiation (Fig. 3 and Fig. 8S in Supplementary data). The overall polymerization results are summarized in Table 4.

As can be seen from these data, all the studied dye/**Tz** photosystems are able to initiate the polymerization process in an air equilibrium composition. However, the free radical polymerization initiated by the tested photoredox pairs showed a significant inhibition time (Fig. 3 and Table 4). This effect should be related to the molecular oxygen dissolved in the composition. The oxygen both quenched the triplet state of the dye and reacted with the radical species generated by the dye/**Tz** systems. After consumption of the oxygen, the initiating radicals reacted with the monomer. As seen in Table 4, the most efficient photoredox pair, **6c/Tz**, had the shortest inhibition time (Fig. 4).

Moreover, the calculated polymerization rate (R_p) presented in Table 4, indicated that the efficiency of polymerization strongly depended upon the structure of the dye employed. It was apparent that dyes **6c** and **4a** significantly accelerated the triacrylate photopolymerization in comparison to the other dyes studied. It is well known [30] that the R_p for polymerization initiated via intermolecular electron transfer process can be described by Eq. (5).



Fig. 2. Oxidation potentials of the compounds 7–13 as a function of the IP_{gas} (R = 0.95).



Fig. 3. Kinetic curves of TMPTA photopolymerization recorded under an air atmosphere for **Tz** and dyes **4b** (\blacksquare), **6b** (\blacksquare), **6c** (\bigcirc) and **6e** (\blacktriangle).



Fig. 4. Relationship between inhibition time and the rate of photoinitiated polymerization initiated by the dye/**Tz** systems (R = 0.86).



Fig. 5. Marcus plot of the rates of polymerization initiated by the dye/Tz systems.

$$\ln R_{\rm p} = A - \frac{\lambda \left(1 + \frac{\Delta G_{\rm et}}{\lambda}\right)^2}{4RT}$$
(5)

where A is a constant, which is dependent on the intensity of absorbed light (I_a), the quantum yield of triplet state formation (Φ_T), the rate constants of polymerization (k_p) and chain termination steps (k_t), and the concentration of monomer and co-initiators. The detailed review of the experimental data presented in Table 4 reveals a parabolic relationship between the logarithm of R_p and the thermodynamic parameter ΔG_{et} (Fig. 5). This indicates that the rate of electron transfer between the studied dyes and **Tz** is a limiting step for photoinitiated polymerization [30].

4. Conclusions

Novel dyes based on the dithiinoquinoxaline skeleton were successfully synthesized and characterized using ¹H NMR and CI MS spectroscopy. These new dyes, when combined with 2,4,6-tris(trichloromethyl)-1,3,5-triazine (**Tz**), may have practical applications as visible-light photoinitiators of free radical polymerization. The ability of dye/**Tz** systems to act as a photoinitiator strongly depended upon the free energy change of the intermolecular photoinduced electron transfer from the excited dyes **4** and **6** to the co-initiator. The limiting step in the photoinitiated polymerization of TMPTA by dye/ **Tz** systems is an electron transfer within the photoredox pair.

Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.dyepig.2011.09.006.

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