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The photochemical behaviour of naphthoylenebenzimidazolone dyes in 1-methyl-2-pyrrolidone

Jolanta Kolińska [a], Radosław Podsiadły [a], Stanisław Wysocki [b], Jolanta Sokołowska [a,*]

[a] Institute of Polymer and Dye Technology, Technical University of Lodz, Stefanowskiego 12/16, 90-924 Lodz, Poland
[b] Department of Food Sciences and Biotechnology, Technical University of Lodz Stefanowskiego 4/10, 90-924 Lodz, Poland

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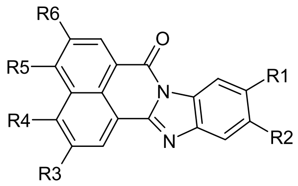
ABSTRACT

The photochemical behaviour of selected naphthoylenebenzimidazolone dyes is discussed in terms of the photobleaching of the dyes in the presence of electron donors (phenylthioacetic acid, *N*-phenylglycine, ethyl 4-*N*,*N*-dimethylaminobenzoate) as well as an electron acceptor (1-methoxy-4-phenylpyridinium tetrafluoroborate) that are used in photoredox systems for light-induced polymerization. The fluorescence quenching of the dyes in the presence of the electron donors and the electron acceptor was also examined.

1. Introduction

Light-induced polymerization of multifunctional acrylates and methacrylates is used in industrial coatings, composites and adhesives [1–3]. Many early photoinitiating systems were sensitive to UV light, but a large number of systems have been developed to extend these early systems' spectral sensitivity to the visible range. The latter process requires the presence of the absorptive dye participating in a photoinduced electron transfer (PET) process [4–6]. In this process, the dye may be photoreduced [7–9] in the presence of suitable reductants (such as phenylthioacetic acid – PhSAc, *N*-phenylglycine – NPhGly, or ethyl 4-*N*,*N*-dimethylaminobenzoate – DMB) or photooxidized [10] by a strong electron acceptor such as alkoxypyridinium salt (e.g., 1-methoxy-4-phenylpyridinium tetrafluoroborate – Py1) [11]. These processes are presented in Schemes 1–3.

The aim of this study was to investigate the photochemical properties of naphthoylenebenzimidazolone dyes (**1**–**17**) combined in photoredox pairs with electron donors or acceptors that have previously been used for photoinduced polymerization processes [12,13]. The processes occurring in these photoredox systems are illustrated in Schemes 4–6. In particular, the photobleaching of the dyes and their fluorescence quenching in the presence of selected electron donors and an electron acceptor are discussed.



Dye	R1	R2	R3	R4	R5	R6
1	H	H	H	H	H	H
2	CH_3	CH_3	H	H	H	H
3	Cl	Cl	H	H	H	H
4	Cl	H	H	H	H	H
5	H	Cl	H	H	H	H
6	Br	H	H	H	H	H
7	H	Br	H	H	H	H
8	H	H	H	H	Br	H
9	H	H	H	Br	H	H
10	H	H	Br	H	H	H
11	H	H	H	H	H	Br
12	CH_3	CH_3	Br	H	H	H
13	CH_3	CH_3	H	H	H	Br
14	Cl	Cl	Br	H	H	H
15	Cl	Cl	H	H	H	Br
16	H	H	H	Cl	Cl	H
17	H	H	H	Br	Br	H

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* Corresponding author. Tel.: +48 42 6313232.
E-mail address: jsokolow@p.lodz.pl (J. Sokołowska).

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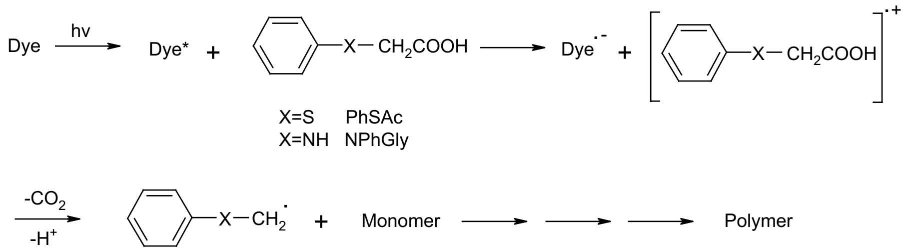
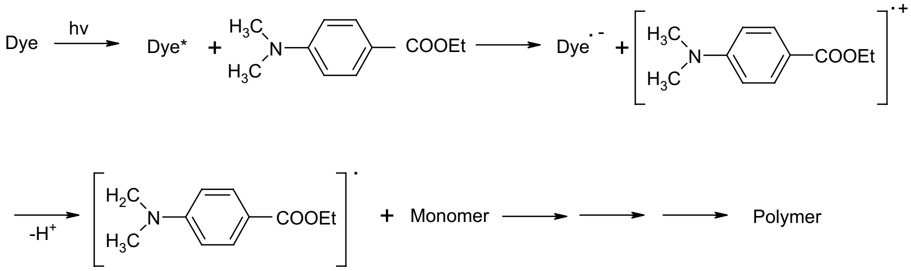
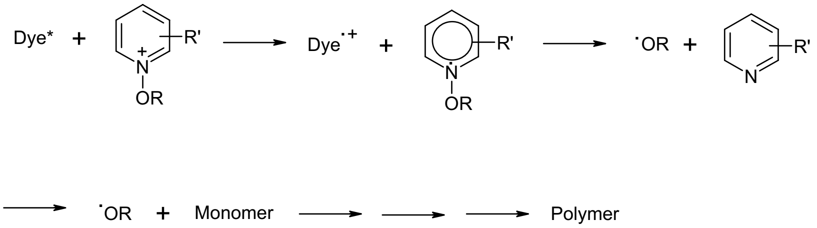


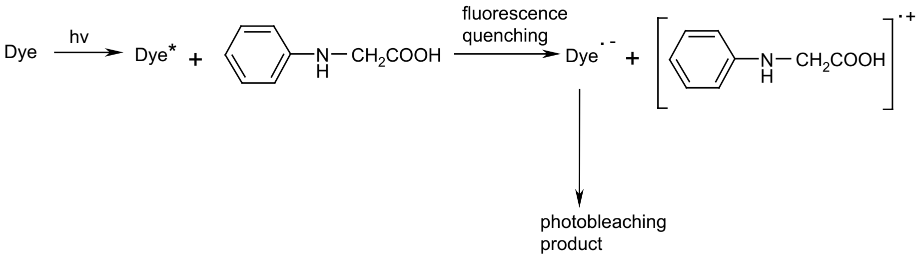
Scheme 1.



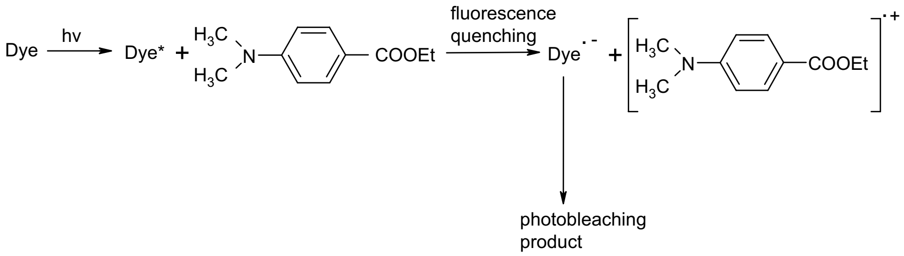
Scheme 2.



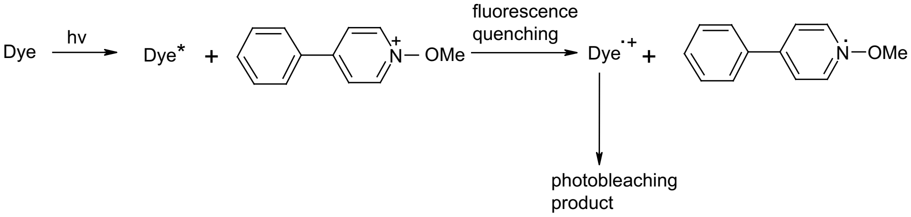
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

Table 1
Spectroscopic,[a] photophysical[a] and electrochemical properties[b,c] of dyes **1–17.**

Dye	λ_{max}, nm	λ_{em}, nm	Singlet lifetime, ns	Φ_{Fl}	$E^{ox}_{1/2}$, V	$E^{red}_{1/2}$, V
1	392	508	9.09	0.30	0.62[b]	−1.62[b]
2	400	534	5.49	0.22	0.61[b]	−1.68[b]
3	384	501	9.25	0.41	0.61[b]	−1.45[b]
4	387	497	6.00	0.32	0.64[b]	−1.57[b]
5	383	492	7.40	0.45	0.69[b]	−1.52[b]
6	389	504	5.34	0.29	0.66[b]	−1.61[b]
7	381	485	6.20	0.28	0.66[b]	−1.59[b]
8	392	507	7.31	0.35	0.60[b]	−1.55[b]
9	383	513	7.56	0.19	0.59[b]	−1.50[b]
10	391	509	8.13	0.33	0.86[c]	−1.25[c]
11	396	529	5.80	0.21	0.85[c]	−1.22[c]
12	409	549	5.86	0.21	0.99[c]	−1.27[c]
13	406	537	7.00	0.11	0.89[c]	−1.27[c]
14	380	496	5.84	0.28	0.84[c]	−1.13[c]
15	391	502	5.81	0.19	0.62[c]	−0.96[c]
16	404	526	6.66	0.39	0.99[c]	−1.09[c]
17	407	507	8.26	0.24	0.90[c]	−1.05[c]

[a] In 1-methyl-2-pyrrolidone from ref. [12].
[b] In CH_3CN from Ref. [12].
[c] In DMF.

2. Experimental

Both the electron acceptor and electron donors were purchased from Aldrich (Poland). The dyes were synthesized using the procedure previously described [12,13]. Absorption and fluorescence spectra in 1-methyl-2-pyrrolidone were recorded using a Perkin Elmer Lambda 40 spectrophotometer (USA) and a Fluoromax-2 spectrofluorimeter (Horiba Jobin Yvon Inc., USA), respectively.

2.1. *Electrochemical experiments*

The electrochemical experiments were carried out in acetonitrile (**1–9**) or DMF (**10–17**) containing 0.1 mol tetra-n-butylammonium perchlorate as the supporting electrolyte. All solutions were degassed prior to experiments by bubbling with argon. During each experiment, a blanket of argon was maintained over the solution. The substrate concentration (dye or electron acceptor/donor) was 1×10^{-3} mol dm^{-3}. Staircase voltammetry (SCV) was used for measurements, with the potential provided by a commercially-available potentiostat (AUTOLAB, Ecochemie, Holland). Platinum was used for both the working and the auxiliary electrodes. Ferrocene was used as the reference electrode [14].

2.2. *Photochemical experiments*

All bleaching experiments were performed in a Rayonet RPR 200 Reactor (the Southern New England Ultraviolet Co, USA) equipped with eight lamps emitting light at 419 nm. These processes were carried out in 1-methyl-2-pyrrolidone solution under nitrogen. Illumination intensity was measured using uranyl oxalate actinometry [15], with the extent of dye fading determined based on the decrease in absorption at λ_{max}. The quantum yield of dye bleaching Φ_{bl} was calculated from at least three determinations, with the reaction carried out for 120 s.

Stern–Volmer constants were obtained from fluorescence quenching experiments. The fluorescence spectra of dye solutions (≈ 10 μM) in 1-methyl-2-pyrrolidone containing various amounts of quenchers were measured at room temperature in an air atmosphere using excitation at λ_{max}.

Table 2
Characteristics of dye/electron donor and dye/electron acceptor photoredox pairs.

Dye	PhSAc		DMB		NPhGly		Φ_{bl} with NPhGly, mmol quant^{-1}	Py1		Φ_{bl} with Py1, mmol quant^{-1}
	K_{SV}, M^{-1}	$k_q \times 10^{-10}$ M^{-1} s^{-1}	K_{SV}, M^{-1}	$k_q \times 10^{-10}$, M^{-1} s^{-1}	K_{SV}, M^{-1}	$k_q \times 10^{-10}$, M^{-1} s^{-1}		K_{SV}, M^{-1}	$k_q \times 10^{-10}$, M^{-1} s^{-1}	
1	–	–	20.05	0.22	162.06	1.78	2.27	–	–	3.90
2	–	–	24.08	0.44	94.86	1.73	1.39	–	–	2.68
3	–	–	19.83	0.22	289.74	3.13	1.27	39.19	0.42	3.96
4	–	–	33.74	0.56	183.52	3.06	2.50	5.61	0.10	3.38
5	12.31	0.17	64.97	0.88	314.56	4.25	1.63	18.55	0.25	4.09
6	7.85	0.15	17.77	0.33	256.21	4.80	3.54	82.40	1.54	4.10
7	–	–	36.60	0.59	131.52	2.12	3.48	15.68	0.25	4.76
8	9.53	0.13	39.90	0.55	150.40	2.06	3.52	–	–	3.32
9	–	–	42.30	0.56	96.84	1.28	2.18	–	–	3.03
10	–	–	21.80	0.27	150.76	1.85	2.88	8.74	0.11	1.82
11	7.12	0.12	17.99	0.31	158.03	2.73	1.17	–	–	1.90
12	–	–	19.95	0.34	86.72	1.48	1.84	6.31	0.11	1.52
13	21.03	0.30	27.80	0.40	55.76	0.80	2.99	–	–	0.82
14	–	–	12.04	0.21	126.86	2.17	1.18	–	–	1.92
15	28.21	0.49	41.34	0.71	127.59	2.20	1.82	16.85	0.29	4.10
16	14.60	0.22	47.52	0.72	82.60	1.24	1.32	*	*	1.06
17	–	–	38.27	0.55	42.80	0.62	4.10	–	–	0.93

Light intensity (419 nm): 1.6×10^{17} quant s^{-1}. *See text and Fig. 2.

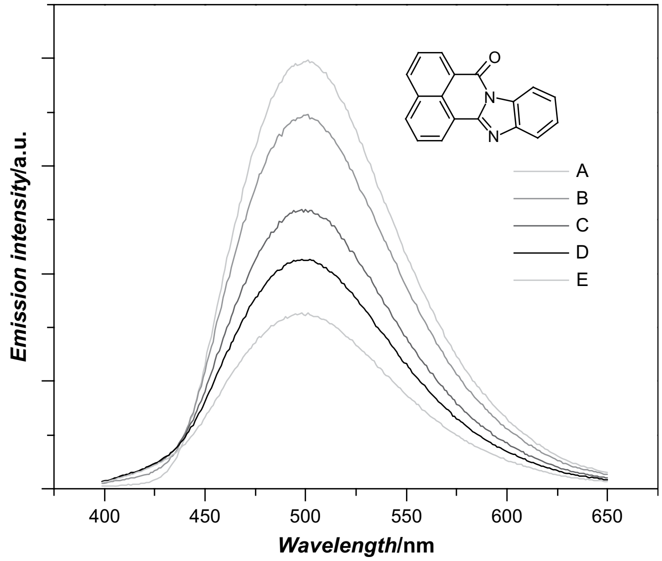


Fig. 1. Fluorescence quenching of dye **1** with NPhGly; (A: the dye without NPhGly; B, C, D, E: the dye with NPhGly at concentrations of 2×10^{-3}, 5×10^{-3}, 7×10^{-3}, 1×10^{-2} mol dm^{-3}, respectively).

The fluorescence quantum yield of the dye (Φ_{dye}) was calculated from equation (1)

$$\Phi_{\text{dye}} = \Phi_{\text{ref}} I_{\text{dye}} A_{\text{ref}} / I_{\text{ref}} A_{\text{dye}} \tag{1}$$

where Φ_{ref} denotes the fluorescence quantum yield of the reference: ($\Phi_{\text{ref}} = 0.8$ [11] in 1-methyl-2-pyrrolidone), A_{dye} and A_{ref} denote the absorbances of the dye and the reference, respectively, at their excitation wavelengths, and I_{dye} and I_{ref} refer to the areas under the fluorescence peaks for the dye and reference, respectively.

Fluorescence lifetime measurements were made using time-correlated single photon counting (Edinburgh Analytical Instruments Co.). The light source was a hydrogen lamp of thyratron with a frequency of 40 kHz. The bandpass was 3.6 nm for both excitation and emission. The instrument response function was recorded by collecting scattered light from a Ludox silica suspension. Fluorescence decay from both the sample and the scattering solution was acquired at 1.0×10^4 counts at the peak intensity. Fluorescence decays were fitted to a sum of exponentials (equation (2)):

$$I(t) = \sum_{i}^{n} \alpha_i \exp(-t/\tau_{\text{i}}) \tag{2}$$

with amplitudes α_{i} and decay lifetimes τ_{i}. The average lifetimes $\langle\tau\rangle$ for bi- or triexponential fluorescence decays were calculated from decay times and preexponential factors using equation (3).

$$\langle\tau\rangle = \sum \alpha_i \tau_i^2 / \sum \alpha_i \tau_i \tag{3}$$

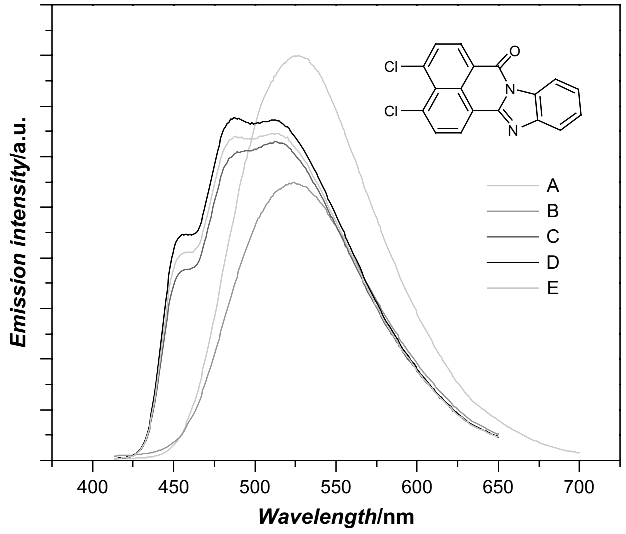


Fig. 2. Fluorescence quenching of dye **16** with Py1: (A: the dye without Py1; B, C, D, E: the dye with NPhGly at concentrations of 2×10^{-3}, 5×10^{-3}, 7×10^{-3}, 1×10^{-2} mol dm^{-3}, respectively).

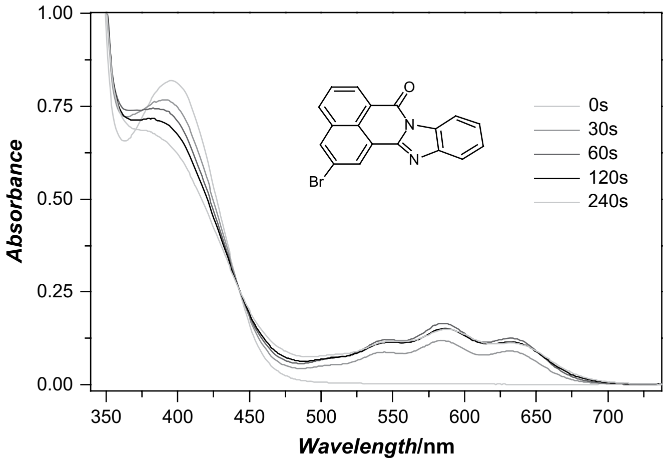


Fig. 3. The bleaching spectrum of dye **10** combined with Py1.

3. Results and discussion

As has already been mentioned, the objective of our study was examination of the photoreactions of photoredox pairs consisting of the dye and electron donor or acceptor, respectively. Schemes 4–6 illustrate the photochemical processes of the dye that may occur with the application of electron donors such as PhSAc, DMB and NPhGly or electron acceptors similar to Py1 in the absence of monomer.

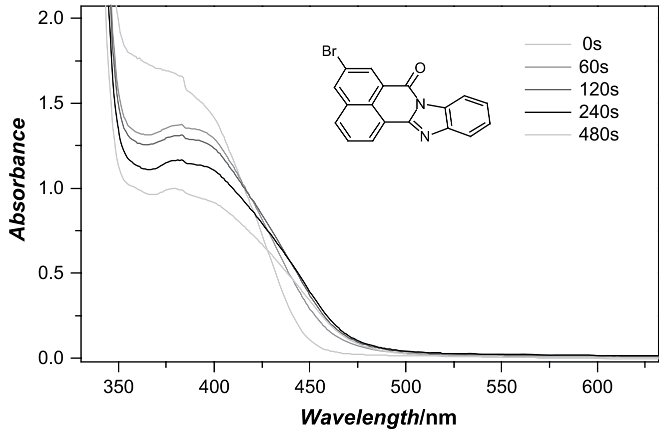


Fig. 4. The bleaching spectrum of dye **11** combined with Py1.

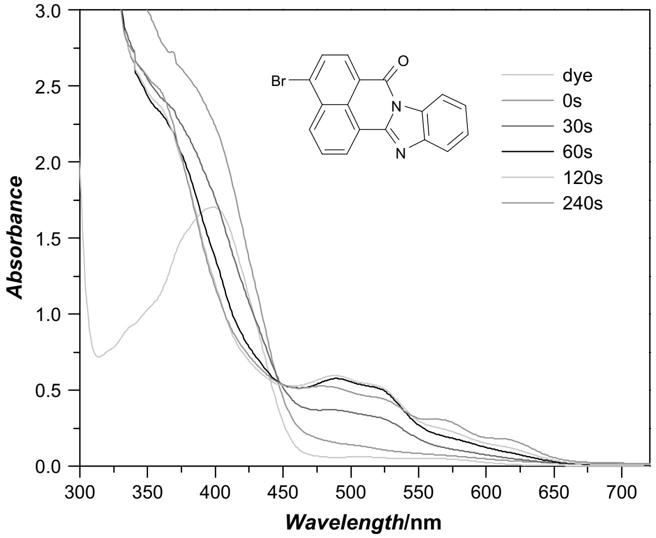
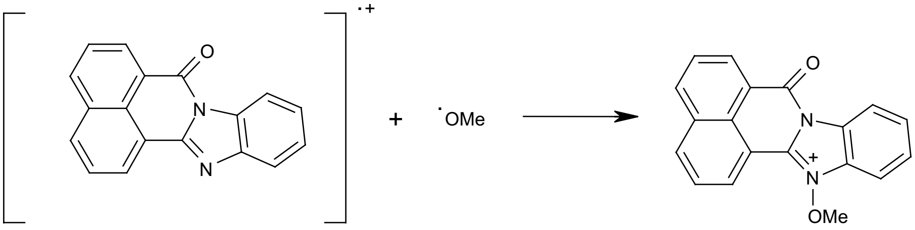


Fig. 5. The bleaching spectrum of dye **8** combined with NPhGly.



Scheme 7.

Spectroscopic properties (i.e., absorption and emission spectra, quantum yield, and the singlet-state lifetime) of the dyes are presented in Table 1. Dyes **1**–**17** absorb between 380 and 420 nm, with their emissions characterized by Stokes shifts of ≈100–133 nm. As can be seen in Table 1, the fluorescence quantum yields of the tested dyes are moderate and range from 0.11 to 0.45, with the highest values seen for dyes containing chlorine. The singlet lifetimes are in the range from 5 to 9 ns, depending on the dye structure. Typically, the dyes containing bromine possess shorter lifetimes probably due to efficient intersystem crossing to triplet states.

Table 2 (dashes mean the lack of measurable quenching) shows the measured values of Stern–Volmer constants (K_{SV}) and calculated singlet quenching constants (k_q). It is evident that the electron donors used in this study effectively quench the fluorescence of naphthoylenebenzimidazolone dyes. The example of fluorescence quenching of dye **1** in the presence of NPhGly is presented in Fig. 1.

All other dyes behave in a similar manner. Moreover, any new peaks observed in their emission spectra preclude exciplex formation. Fluorescence quenching by PhSAc, which has the highest value of $E^{ox}_{1/2}$ (0.78), [12] is limited to a subset of the dyes studied in this work. DMB and NPhGly, which have lower values of $E^{ox}_{1/2}$ (0.68 [12], 0.63 [12], respectively), quench the fluorescence of all dyes used in this research.

The calculated values of k_q, which are close to the diffusion-controlled limit ($k_q \approx 1 \times 10^9$–$1 \times 10^{10}\ M^{-1}\ s^{-1}$), along with the observation that in most cases the dyes with low values of reduction potential have the highest value of k_q, suggest that fluorescence quenching proceeds via an electron transfer process.

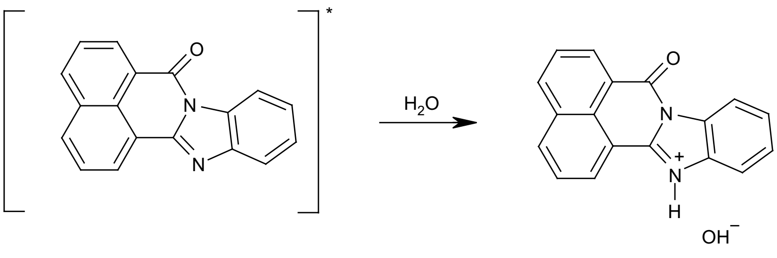
The fluorescence quenching by pyridinium salt Py1 is only limited to a subset of the studied dyes. Additionally, in the case of dye **16**, the process was accompanied by the formation of new product(s) showing a hypsochromic effect on λ_{em} (Fig. 2) when compared to the initial location of λ_{em}.

Singlet quenching constants (k_q) indicate that the quenching process occurs via an electron transfer. As can be seen from Table 2, some dyes (**1**, **2**) do not exhibit fluorescence quenching although they have low values of their $E^{ox}_{1/2}$. Additionally, the same happens in halogen substituted dyes due to intersystem crossing to the triplet state. This suggests that an electron transfer process may proceed via the triplet state of the dye.

In photoinduced polymerization initiated by a photoredox pair, bleaching of the dye is a very important factor – especially if the process must be carried out in thick layers. In the photobleaching study we limited our experiments to the most promising photoredox pairs consisting of the dyes and NPhGly or Py1, respectively.

The photobleaching quantum yields (Φ_{bl}) of the dyes in these selected photoredox pairs are presented in Table 2. Additionally, the detailed bleaching spectra of photoredox pairs containing dyes **10** and **11** combined with pyridinium salt Py1, and dye **8** combined with NPhGly are shown in Figs. 3–5, respectively.

It is evident (Table 2) that dyes **1**–**9** are more readily bleached in the presence of an electron acceptor (Py1), whereas in most cases the bleaching of dyes **10**–**17** proceeds more efficiently in the presence of an electron donor (NPhGly). This is in good agreement with the tendency of the dyes for redox processes, as illustrated by their $E^{red}_{1/2}$ or $E^{ox}_{1/2}$ values.



Scheme 8.

The most important observation of the spectral analysis is that in each case with the exception of dyes **11**, **13** and **15**, the decay of dye absorption in the presence of Py1 is accompanied by the formation of a new red-shifted (≈500–600 nm) absorption band(s), relative to that of the sensitizer. The same phenomenon is observed for all dyes combined with NPhGly during their bleaching tests. Moreover, in the separate experiments we proved that the similar bands were also generated during the illumination of the dyes in 1-methyl-2-pyrrolidone (highly hygroscopic) without any additives. Therefore, we propose the following mechanisms to explain this unusual behaviour.

Schemes 7 and 8 illustrate the reactions which may occur in the presence of Py1 and without any additives, while Scheme 1 (the generation of H^+ in the presence of NPhGly) additionally supports the latter mechanism.

Since our previous investigation [12] found shoulders exhibiting bathrochromic effects in the spectra of cationic dyes, we believe that the products generated under different conditions may also be due to cationic structures.

4. Conclusions

The fluorescence and photobleaching processes of photoredox pairs consisting of naphthoylenebenzimidazolone dyes in combination with PhSAc, NPhGly, DMB (electron donors) and 1-methoxy-4-phenylpyridinium tetrafluoroborate (an electron acceptor) in 1-methyl-2-pyrrolidone were studied. The dyes containing halogens have shorter singlet lifetimes due to intersystem crossing to the triplet state. Among three electron donors, DMB and NPhGly exhibited the best fluorescence quenching. This high rate of fluorescence quenching is likely due to these electron donors' relatively low $E^{ox}_{1/2}$ values. 1-Methoxy-4-phenylpyridinium tetrafluoroborate quenches the fluorescence of the selected dyes, showing efficient quenching in case of some compounds containing halogens. In both cases the values of k_q are close to the diffusion-controlled limit, which suggests that electron transfer processes may play a role in fluorescence quenching. All dyes exhibit bleaching upon irradiation with 419 nm light, which in most cases is accompanied by formation of degradation product(s) which absorb very weakly between 500 and 600 nm.

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