Blue-to-Red Light Sensitive Push—Pull Structured Photoinitiators: Indanedione Derivatives for Radical and Cationic Photopolymerization Reactions

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Supporting Information

ABSTRACT: The actual photonitiators PI can only operate in a restricted part of the visible spectrum; as a consequence, several PIs are usually necessary to harvest all the emitted visible photons. In the present paper, new dyes based on a donor– π acceptor structure (1,3-indanedione derivatives) are incorporated into visible light sensitive photoinitiating systems of polymerization. They exhibit an unusual and remarkable broad absorption lying from the blue to the red. When employed in the presence of an iodonium salt (Iod) and optionally *N*vinylcarbazole (NVK), these dyes can efficiently initiate the radical photopolymerization of acrylates, the cationic photopolymerization of epoxide and vinylether monomers and the hybrid cure of acrylate/epoxide blends under exposure, e.g., at



405, 457, 473, 532, and 635 nm. They partly behave as organic photocatalysts. These particular light absorption properties and the initiation step mechanisms are investigated in detail.

INTRODUCTION

Visible light induced photopolymerization reactions occur in the presence of a colored molecule incorporated into an absorbing photoinitiating systems PIS and being able to act as a photoinitiator PI or a photosensitizer PS.^{1,2} Free radical polymerization FRP as well as cationic polymerization CP and free radical promoted cationic polymerization FRPCP can be easily achieved both under high and low intensity light sources.³ Many dyes incorporating in mono- and multicomponent PIS have been already proposed (see, e.g., an upto-date review in ref 1). Improving the performance attained or meeting new or promising possibilities of applications require a continuous search of new structures. Looking at the literature is quite amazing: despite the fact that more than 50 years of research have led to the possible use of a huge number of PI, PS and PIS, the most recent analysis of the current works in this area shows tremendous and successful efforts deployed by numerous groups for innovative proposals of new dye structures (see examples of recent papers in this field⁴⁻⁷) as exemplified by the recent introduction of colored substituted ketones, modified organometallic derivatives, various series of dyes, light harvesting compounds or multicolor photoinitiators. Nevertheless, there is still a place for the continuous disclosure of new PISs. Following our works in this area,⁷ we explore here the possibility of using push-pull molecules that could exhibit a broad visible absorption and act as photoinitiators of FRP, CP and FRPCP being able to operate under various laser lines.

As known, push-pull molecules consist in unsymmetrically substituted D- π -A arrangements bearing electron donor (D) and electron acceptor (A) functionalities at both ends of a planar conjugated spacer. The push-pull effect which results from the intramolecular donor/acceptor interaction and a favorable orientation of the charge delocalization in the axis of the chromophore is characterized by a strong absorption band detected in the visible region (named intramolecular charge transfer band ICT) whose position is determined not only by the strength of the donor/acceptor pair but also more subtly by the π -conjugated spacer. Push-pull molecules also relate to a particularly interesting class of molecules that shows outstanding transition energy shifts by changing the solvent polarity/polarizability,8 present a remarkable ability to work under two-photon excitations and have been developed for potential applications, e.g., in optics, molecular electronics, optoelectronic devices, dye-sensitized solar cells, etc.; see ref 9.

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Our actual search for new initiating systems for visible light prompts us to develop new dyes based on this D- π -A structure (Scheme 1). They are based on difunctional structures where



an indanedione moiety is linked to an aniline or a pyrene moiety through a CC double bond. Through the ICT, interesting absorptions are expected. ESR experiments, laser flash photolysis, steady state photolysis, absorption spectrum studies and molecular orbital calculations will be carried out. The ability of these photo initiators in FRP, CP and FRPCP reactions upon exposure to laser diodes from 405 to 635 nm will be checked.

EXPERIMENTAL SECTION

i. Synthesis of the Different Photoinitiators. The investigated dyes (D 1 and D 2) shown in the Scheme 1 were prepared according to the following procedures. All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. ¹H and ¹³C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ¹H (400 MHz) and ¹³C (100 MHz). The ¹H chemical shifts were referenced to the solvent peak DMSO-d₆ (2.49 ppm), CDCl₃ (7.26 ppm) and the ¹³C chemical shifts were referenced to the solvent peak DMSO- d_6 (39.5 ppm), CDCl₃ (77 ppm). The two dyes D 1 and D 2 were prepared by Knoevenagel condensation of Indane-1,3-dione with the corresponding aldehyde. All these dyes were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis. The stability and storage of D 1 and D_2 are excellent; these dyes do not need special storage conditions.

Scheme 2

Synthesis of 2-(4-(*N*,*N*-Dimethylamino)Benzylidene)-1H-indene-1,3(2H)-dione, **D_1**. 4-*N*,*N*-Dimethylaminobenzaldehyde (1 g, 6.84 mmol) and indane-1,3-dione (1 g, 6.84 mmol) were suspended in absolute ethanol (20 mL), and a few drops of piperidine were added. Immediately, the solution turned deep red. The solution was refluxed for 4 h. After cooling, the solution was concentrated to 1/5th of its initial volume. Addition of ether precipitated a red solid which was filtered off, washed several times with water and dried under vacuum. ¹H NMR (CDCl₃), δ (ppm): 3.14 (*s*, 6H, N(CH₃)₂), 6.87 (d, 2H, *J* = 8.7 Hz), 7.67 (*s*, 1H), 7.84–7.86 (m, 4H), 8.55 (d, 2H, *J* = 8.7 Hz). ¹³C NMR (CDCl₃), δ (ppm): 40.1, 111.6, 122.2, 134.7, 134.9, 139.0, 141.4, 141.4, 146.5, 154.1, 189.1, 190.5. HRMS (ESI MS) *m*/*z*: theor, 278.1176; found, 278.1178 ([M + H]⁺ detected)

Synthesis of 2-(Pyren-1-ylmethylene)-1H-indene-1,3(2H)-dione, **D_2.** Pyrene 1-carbaldehyde (1.57 g, 6.84 mmol) and indane-1,3-dione (1 g, 6.84 mmol) were suspended in 20 mL of absolute ethanol, and a few drops of piperidine were added. Immediately, the solution turned orange. The solution was refluxed for 3 h. During that time, a precipitate formed. After cooling, the precipitate was filtered off, washed several times with ethanol and ether, and finally dried under vacuum. ¹H NMR (DMSO-*d*₆), δ (ppm): 7.95–8.03 (m, 2H), 8.06–8.14 (m, 2H), 8.19–8.21 (m, 1H), 8.29–8.33 (m, 2H), 8.38–8.53 (m, 5H), 8.58–8.64 (m, 2H). HRMS (ESI MS) *m/z:* theor, 359.10667; found, 359.1066 ([M + H]⁺ detected); Anal. Calcd for C₂₆H₁₄O₂: C, 87.1; H, 3.9; O, 8.9. Found: C, 87.2; H, 4.0; O, 8.8.

ii. Chemical Compounds. *N*-Vinylcarbazole (NVK) and diphenyliodonium hexafluorophosphate (Ph_2I^+ or Iod) were obtained from Aldrich and used with the best purity available (Scheme 2). (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX, Uvacure 1500) and trimethylolpropane triacrylate (TMPTA) were obtained from Cytec (Scheme 2). Triethylene glycol divinyl ether (DVE-3; as a representative of vinyl ether monomers) was obtained from Aldrich and used with the best purity available (Scheme 2). EPOX, DVE-3, and TMPTA were selected as representative monomers: these monomers are well-known in the photopolymerization field and represent excellent structures to evaluate the initiating ability of new photoinitiating systems.

iii. Irradiation Sources. Several lights were used: (i) polychromatic light from a halogen lamp (Fiber-Lite, DC-950; incident light intensity = $I_0 \approx 12 \text{ mW cm}^{-2}$, in the 370–800 nm range); (ii) monochromatic light delivered by laser diodes at 457, 473, 532, and 635 nm (MBL-III-BFIOPTILAS; $I_0 \approx 100 \text{ mW cm}^{-2}$). A laser diode at 405 nm was also used ($I_0 \approx 12 \text{ mW cm}^{-2}$). The emission spectra for these several lights are given in.¹⁰

iv. Free Radical Photopolymerization (FRP) Experiments. Trimethylolpropane triacrylate (TMPTA from Cytec) was used as a low viscosity monomer. The experiments were carried out in laminated conditions. The films (25 μ m thick) deposited on a BaF₂ pellet were irradiated (see the section Irradiation Sources). The evolution of the double bond content was continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 1630 cm⁻¹



as in ref 11. The polymerization of TMPTA can also be observed at about 1408 $\rm cm^{-1}.$

v. Cationic Polymerization (CP) and Free Radical Promoted Cationic Polymerization (FRPCP). The two- and three-component photoinitiating systems are based on dye/iodonium salt (0.3%/2% w/w) and dye/iodonium salt/NVK (0.3%/2%/3% w/w), respectively. The experimental conditions are given in the Figure captions. The residual weight content is related to the monomer. The photosensitive formulations (25μ m thick) were deposited on a BaF₂ pellet under air (or in laminated conditions for DVE-3; DVE-3 is a very low viscosity monomer: polymerization must be carried out in laminated conditions to avoid a change of thickness). The evolution of the epoxy group (for EPOX) and the double bond (for vinyl ether monomer) contents were continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 790 and 1619 cm⁻¹, respectively.

vi. Computational Procedure. Molecular orbital calculations were carried out with the Gaussian 03 suite of programs. The electronic absorption spectra for the different compounds were calculated with the time-dependent density functional theory at B3LYP/6-31G* level on the relaxed geometries calculated at UB3LYP/6-31G* level.

vii. ESR Spin Trapping (ESR-ST) Experiments. The ESR-ST experiments were carried out using an X-Band spectrometer (MS 400 Magnettech). The radicals were produced at RT under a halogen lamp exposure under N_2 and trapped by phenyl-*N*-tert-butylnitrone (PBN) according to a procedure described in detail in refs 12 and 13. The ESR spectra simulations were carried out with the PEST WINSIM program.

viii. Fluorescence Experiments. The fluorescence properties of the compounds were studied using a JASCO FP-750 spectrometer.

ix. Redox Potentials. The redox potentials were measured in acetonitrile by cyclic voltammetry with tetrabutyl-ammonium hexafluorophosphate 0.1 M as a supporting electrolyte. The free energy change $\Delta G_{\rm et}$ for an electron transfer reaction is calculated from the classical Rehm–Weller equation (eq 1)¹⁴ where $E_{\rm ox}$, $E_{\rm red}$, $E_{\rm T}$, and C are the oxidation potential of the donor, the reduction potential of the acceptor, the excited state energy and the Coulombic term for the initially formed ion pair, respectively. C is neglected as usually done in polar solvents.¹⁵

$$\Delta G_{\rm et} = E_{\rm ox} - E_{\rm red} - E_{\rm T} + C \tag{1}$$

x. Laser Flash Photolysis. Nanosecond laser flash photolysis (LFP) experiments were carried out using a Qswitched nanosecond Nd/YAG laser (λ_{exc} = 355 nm, 9 ns pulses; energy reduced down to 10 mJ) from Continuum (Minilite) and an analyzing system consisting of a ceramic xenon lamp, a monochromator, a fast photomultiplier and a transient digitizer (Luzchem LFP 212).¹⁰

RESULTS AND DISCUSSION

1. Absorption Properties of the New Dyes (D_1 and D_2). The ground state absorption spectra of the proposed indanedione derivatives (the best one being D_1) allow a large and efficient matching with the light source emission spectra (halogen lamp and laser diodes at 405, 457, 473, 532, or 635 nm). Remarkably, high molar extinction coefficients are determined (about 38 000 and 21 000 $M^{-1}cm^{-1}$ for D_1 and D_2 at ~478 and ~464 nm, respectively; ~ 8000 $M^{-1}cm^{-1}$ for D_1 at ~635 nm; Figure 1) compared to absorption only in the UV range for the indanedione, aniline and pyrene moieties. This shows that an important charge transfer occurs in the electronic transition. The spectrum of D_1 is unchanged with the concentration even for very low concentrations (Figure S1 in the Supporting Information); i.e., the presence of absorption bands associated with dimers can be ruled out.

Molecular orbital MO calculations (using the time-dependent density functional theory at B3LYP/6-31G* level on the relaxed geometries calculated at UB3LYP/6-31G* level) show



Figure 1. (A) UV-visible absorption spectra of the different new dyes $(D_1 \text{ and } D_2)$ in acetonitrile; (B) HOMO and LUMO for D_1 (at B3LYP/6-31G* level).

that the lowest energy transition involves strongly delocalized HOMO and LUMO for both dyes (Figure 1B) ($\pi \rightarrow \pi^*$ character). For **D_1**, the HOMO and LUMO are mainly localized on amine and indanedione fragment, respectively. This highlights a charge transfer character in agreement with the push-pull character of this structure

In order to support the presence of this charge transfer character, their solvatochromic behaviors were investigated in seven solvents of different polarities. Indeed, push-pull molecules represent a particularly interesting class of molecules that shows outstanding transition energy shifts by changing the solvent polarity/polarizability.⁸ Results are summarized in the Table 1. Over the years, several empirical polarity scales were developed to investigate the solvatochromism, and different empirical solvent polarity scale, i.e., Dimroth-Reichardt's,16 Kamlet-Taft's,¹⁷ Catalan's,¹⁸ Lippert-Mataga's,¹⁹ Bakhshiev's,²⁰ Kawski–Chamma–Viallet's,²¹ McRae's,²² and Suppan's scales,²³ among others, were reported. Intramolecular nature of the observed charge transfer can be easily demonstrated by realizing successive dilutions, intermolecular charge transfer disappearing at low concentration. If an increase of the Stoke shift can be observed for D 2 with the solvents polarity, an irregular behavior was evidenced for D 1 and no correlation could be established in first approximation (see Table 1). Noticeably, halogenated solvents gave larger absorption wavelengths than nonhalogenated solvents of similar ε values for the two dyes and this unusual trend in halogenated solvents is well-reported in the literature.^{8b,24}

While plotting the Stoke's shift values against the Dimroth– Reichardt solvent parameters or the empirical Kamlet–Taft

Table 1. Absorption and Emission Maxima (nm) Obtained Experimentally by UV–Visible Spectroscopy and Fluorescence Spectroscopy for Dyes D_1 and D_2

solvent	dielectric constant (ε)	refractive index (n)	$\lambda_{\max} (D_1)$	$\lambda_{\rm em}$ (D_1)	Stoke shift	λ_{\max} (D_2)	$\lambda_{\rm em}$ (D_2)	Stoke shift
toluene	2.4	1.497	600	662	62	482	521	39
chloroform	4.8	1.446	620	700	80	487	534	47
THF	7.4	1.407	607	685	78	471	530	59
CH_2Cl_2	8.9	1.424	616	700	84	478	540	62
acetone	20.6	1.359	610	n.e. ^a	-	466	546	80
methanol	32.7	1.328	629	710	81	472	560	88
acetonitrile	37.5	1.344	616	n.e.	-	463	554	91

^an.e.: non-evaluated (too weak to be measured).





parameters, no reasonable linear correlations could be obtained for the two dyes. On the other hand, Lippert–Mataga's, Bakhshiev's, Kawski–Chamma–Viallet's, McRae',s and Suppan's polarity scales all based on both the dielectric constant and the refractive index of the solvents gave remarkable correlations for D_2 (see Figure 2). In particular, the strong negative slopes obtained with the different plots are indicative of significant charge redistribution upon photoexcitation. As anticipated, the largest magnitude of the Stokes shift was observed in the most polar solvents and this variation is indicative of a major change in the dipole moment value referring to a geometry of the excited state different to that of the ground state. Surprisingly, the solvatochromic behavior of D_1 was markedly less linear, as illustrated in the Figure 3. This unexpected behavior can be assigned to the dynamical solute– solvent interactions that take place in solution and to the strong donating ability of the dimethylaminobenzene moiety rendering to some extend this chromophore more sensitive to the polarity/polarizability of the solvents than D_2 only possessing a weak electron donor. In particular, for a given solvent, competing effects of polarity/polarizability and hydrogen bond donating/accepting abilities of opposite forces can also be observed rendering the solvatochromism of D_1 more difficult to anticipate (see Figure 4).

2. Cationic Photopolymerization. *a. Photopolymerization of EPOX.* Using the dye/Iod system, a ring-opening polymerization ROP of EPOX under air is clearly observed (e.g., with D_1/Iod under the laser diode irradiation at 473 nm



Figure 3. Bakhshiev's (a), Kawski–Chamma–Viallet's (b), Lippert–Mataga (c), McRae's (d), and Suppan's (e) solvatochromic correlation plots for D_1 in seven solvents of different polarities and R^2 of the corresponding linear regressions.



Figure 4. Competitive solvatochromic effects affecting the solvatochromism of D_1.

and the halogen lamp; Figure 5; no ROP in the presence of Iod or the dye alone). A very fast photopolymerization and very high final conversions are reached upon addition of NVK (Figure 5A,B, curve 1 vs curve 2; presence of $D_1/NVK/Iod$); final tack free coatings are obtained, e.g., within 6 min of irradiation. A high NVK consumption is noted (i.e., Figure 5A); the formation of the polyether network (as characterized by its absorption band at 1080 cm⁻¹ i.e. Figure 5B) is evidenced. On the opposite, no ROP occurs in the presence of $D_2/Iod/NVK$ (Figure 5A, curve 3). This trend of reactivity does not follow the light absorption properties of the two dyes as D_2 is also

characterized by an excellent light absorption in the visible range (Figure 1).

The efficiency of **D_1**/NVK/Iod under the selected laser diode irradiations decreases in the series (405 nm <635 nm ~532 nm< 457 nm< 473 nm—see Figure 6). This trend of reactivity is in agreement with the light absorption properties of **D_1** at the different laser diode irradiations (Table 2; see the respective absorbed light intensity I_{abs}), i.e., the best polymerization profiles are observed at 473 and 457 nm in agreement with very high extinction coefficients and high diode light intensity. At 405 nm, a slower polymerization process is found; this is ascribed to the low light intensity of the laser diode (Table 2). Interestingly for the different irradiation wavelengths, final conversions >40% are always found.

b. Photopolymerization of DVE-3. The photopolymerization of DVE-3 was carried out in laminated conditions at 473 nm. **D_1** or Iod alone does not lead to any polymerization (Figure 7 curves 1 and 2). In the presence of the twocomponent **D_1**/Iod photoinitiating system, an excellent polymerization is already noted with a conversion about 95% after 30 s of irradiation. The difference between the DVE-3 vs the EPOX profiles should be ascribed to the faster polymerization reactions usually observed with vinyl ethers rather than to a specific effect of the photoinitiating systems (as in^{1,2}).

3. Free Radical Photopolymerization. The best typical conversion-time profiles of trimethylolpropane triacrylate (TMPTA) in laminated conditions under, e.g., a laser diode



Figure 5. Photopolymerization profiles of EPOX under air. (A) Upon a laser diode exposure at 473 nm in the presence of (1) D_1 /Iod (0.3%/2% w/w), (2) D_1 /NVK/Iod (0.3%/3%/2% w/w), and (3) D_2 /NVK/Iod (0.3%/3%/2% w/w). Inset: NVK conversion during the photopolymerization of (2). (B) Upon a halogen lamp irradiation in the presence of (1) D_1 /Iod (0.3%/2% w/w) and (2) D_1 /NVK/Iod (0.3%/3%/2% w/w). Inset: IR spectra recorded during the photopolymerization of 2.



Figure 6. Photopolymerization profiles of EPOX under air in the presence of $D_1/NVK/Iod$ (0.3%/3%/2% w/w): upon different laser diodes exposure at (1) 457, (2) 473, (3) 532, (4) 635, and (5) 405 nm.

Table 2. Molar Extinction Coefficients ε of D_1 at Selected Laser Diode Emission Wavelengths^{*a*}

λ (nm)	$\varepsilon ~(\mathrm{M^{-1}~cm^{-1}})$	$I_0 (\mathrm{mW/cm}^2)$	$I_{\rm abs}$
405	7200	12	4
457	29000	100	81
473	38000	100	88
532	4600	100	23
635	8000	100	36

^{*a*} In acetonitrile. Emission light intensity of the laser diodes used in this work (I_0); absorbed light intensity (I_{abs} in a.u.) for **D_1** (1% w/w) under the selected polymerization conditions (evaluated from $I_{abs} = I_0(1 - 10^{-v[\mathbf{D}_1]!})$).

irradiation at 473 nm are shown in Figure 8. A relatively low final conversion is obtained when using D_1/Iod (Figure 8 curve 1) whereas a better polymerization profiles is reached upon addition of NVK (final conversion ~50% with $D_1/Iod/NVK$; Figure 8 curve 2; final tack-free coating within 4 min).



Figure 7. Photopolymerization profiles of DVE-3 in laminate. Upon the laser diode exposure at 473 nm in the presence of (1) D_{-1} (0.3% w/w), (2) Iod (2% w/w), and (3) D_{-1} /Iod (0.3%/2% w/w).

The same holds true when using a halogen lamp irradiation with $D_1/NVK/Iod$ (Figure S2 in the Supporting Information: final conversion >45%; tack-free coating). As previously for ROP process, D_2 is not found to be an efficient sensitizer for FRP of acrylates; the reactivity of D_2 vs D_1 will be discussed below.

4. Hybrid Cure: Photopolymerization of TMPTA/EPOX Blends. A concomitant radical/cationic polymerization of a TMPTA/EPOX blend (50%/50% w/w) readily occurs in a one-step hybrid cure procedure (e.g., upon exposure at 473 nm; Figure 9; **D**_1/NVK/Iod system). A tack free coating is also obtained after only 6 min of irradiation. Under laminated conditions, the acrylate and epoxide conversions are ~70% and ~40% at t = 400 s, respectively. Tack free coatings can also be obtained under air.

5/. Chemical Mechanisms for D_1 and D_2 . When exposed to the laser diode at 473 nm, a very fast bleaching of the D 1/Iod solution is found (Figure 10). It results (r1) from



Figure 8. Photopolymerization profiles of TMPTA in laminated conditions upon a laser diode exposure at 473 nm in the presence of (1) $D_1/Iod (0.3\%/2\% \text{ w/w})$ and (2) $D_1/NVK/Iod (0.3\%/3\%/2\% \text{ w/w})$.



Figure 9. Photopolymerization profiles of a TMPTA/EPOX blend (50%/50%) in laminated conditions using $D_1/NVK/Iod$ (0.3%/ 3%/ 2% w/w). The evolutions of the acrylate and epoxide functions were followed as presented in ref 10.

the oxidation of **D_1** by Iod leading to PhI, $(\mathbf{D_1})^{\bullet+}$ and a phenyl radical Ph[•] (originating from the subsequent very fast cleavage of Ph₂I[•] in eq r2)¹ as supported by ESR-ST and ESR experiments. Ph[•] (Figure 11A) and **D_1**^{•+} (Figure 11B) are

clearly observed: the hyperfine coupling constants hfc ($a_{\rm N} = 14.2$ G; $a_{\rm H} = 2.2$ G) agree with the known data for the PBN/ Ph[•] adduct;^{12,13} the radical cation is characterized by a distinct singlet signal with $g \sim 2.003$ in agreement with ref 25. Upon identical light absorbed intensity, **D_1** is more reactive than **D_2**: indeed, the photolysis of the **D_1**/Iod solution is much faster than that of **D_2**/Iod (Figure 10B vs Figure 10A). The lower photolysis of **D_2**/Iod can be explained by a back electron transfer in r1 regenerating the starting compounds. Such a deactivation pathway decreases the yield in Ph[•] and **D_1^{•+}** in line with the very low efficiency of the **D_2** based systems in polymerization experiments (see below).

The free energy change $\Delta G_{\rm et}$ for the ¹dye/Ph₂I⁺ electron transfer reaction is favorable according to the redox properties of the reactants (e.g., $E_{\rm ox} = 0.92$ and 1.34 V for **D_1** and **D_2**, respectively [from this work; see Figure 12A]; $E_{\rm red}(Ph_2I^+) \sim -0.2$ V¹; E(¹**D_1**) ~ 1.85 eV (Figure 12B) and $E(^{1}\mathbf{D_2}) \sim 2.47$ eV – from fluorescence experiments; free energy change $\Delta G = -0.73$ eV and -0.93 eV for **D_1** and **D_2**, respectively). In laser flash photolysis experiments, no transient ascribable to a triplet state can be observed for **D_1** in agreement with a S₁ pathway.

As usually,²⁶ these phenyl radicals (Ph[•]) are easily converted into NVK radicals (NVK[•]) by an addition to the double bond of NVK (r3). The formation of the NVK radicals (NVK[•]) upon irradiation of $D_1/Ph_2l^+/NVK$ ($a_N = 14.3$ G; $a_H = 2.5$ G in agreement with^{13,26}) is also observed (Figure 11C). As previously discussed in other related systems,^{26,27} the NVK⁺ cations are easily formed (r4, r5) and will initiate the ROP of the epoxide. Reaction r5 allows a regeneration of the dye and brings an interesting photocatalyst character to D_1 . For cationic polymerization, dye^{•+} and Ph-NVK⁺ are the initiating species whereas Ph[•] and Ph-NVK[•] can initiated free radical polymerization.

dye
$$\rightarrow$$
 ¹dye (h ν)

¹dye + Ph₂I⁺ \rightarrow dye^{•+} + Ph[•] + Ph - I (r1)

$$Ph_2I^{\bullet} \to Ph^{\bullet} + Ph - I$$
 (r2)

$$Ph^{\bullet} + NVK \to Ph - NVK^{\bullet}$$
(r3)

$$Ph - NVK^{\bullet} + Ph_2I^+ \rightarrow Ph - NVK^+ + Ph - I + Ph^{\bullet}$$
(r4a)



Figure 10. Photolysis of D_1/Iod (A) or D_2/Iod (B) in acetonitrile, under air; laser diode exposure at 473 nm (identical light absorption intensity); [Iod] = 0.04 M. The UV-visible spectra were recorded at the same irradiation times; for curve B, all the spectra are superposed.



Figure 11. (A) ESR-spin trapping spectrum of D_1/Iod ; [Iod] = 0.01 M. (B) ESR spectrum of the cation radical $(D_1)^{\Phi^+}$ at room temperature. (C) ESR-spin trapping spectrum of $D_1/Iod/NVK$ in *tert*-butylbenzene. Laser diode exposure at 473 nm. Experimental (a) and simulated (b) spectra. Phenyl-*N*-*tert*-butylnitrone (PBN) is used as spin trap, under N₂.



Figure 12. (A) Cyclic voltammogram for D 1 in acetonitrile. (B) (a) Absorption and (b) fluorescence spectra for D 2.

$$Ph - NVK^{\bullet} + dye^{\bullet +} \rightarrow Ph - NVK^{+} + dye$$
 (r4b)

$$Ph - NVK^{+} + M \rightarrow Ph - NVK - M^{+}$$
(r5)

CONCLUSION

In the present paper, original difunctional dyes exhibiting a push—pull molecular character have been proposed as a new series of photoinitiators. Their own unusual broad absorption lying from the blue to the red allows polymerization reactions under various laser diodes between 405 and 635 nm or low light intensity visible light sources (for example, a halogen lamp or a LED bulb). The free radical polymerization of a low viscosity acrylate monomer (TMPTA), the cationic polymerization of vinyl ethers and epoxides and the radical/cationic hybrid cure of acrylate/epoxide blends are feasible. The synthesis of these dyes is relatively easy, their shell life stability is good and their solubility in organic formulations is excellent. These push—pull structurally tailor-made compounds probably open a new route for the design of multicolor photoinitiators and the development of high performance panchromatic monomer/oligomer films: works are under progress.

ASSOCIATED CONTENT

S Supporting Information

Figure S1, UV–visible absorption spectra of **D_1** for different concentrations, and Figure S2, photopolymerization profiles of TMPTA in laminated conditions upon a halogen lamp irradiation in the presence of **D** $1/\text{Ph}_2\text{I}^+$ or **D** 1/NVK/

 Ph_2I^+ . This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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