

# Diketopyrrolopyrrole dyes: Structure/reactivity/efficiency relationship in photoinitiating systems upon visible lights



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## ABSTRACT

Several diketopyrrolopyrrole derivative based dyes (DPP), combined with an iodonium salt or an amine (and optionally an additive), are studied as photoinitiating systems for the cationic polymerization CP of epoxides or the free radical polymerization FRP of acrylates under different irradiation sources *i.e.* a very soft halogen lamp as well as laser diodes at 473 nm (blue light) and 532 nm (green light). The diketopyrrolopyrrole-furan derivative (**FuDPP**) is very efficient in CP. The structure/reactivity/efficiency relationships in this series of DPP derivatives are investigated. A comparison with a well known reference for visible light photoinitiating system (*i.e.* camphorquinone based photoinitiating system) is also provided showing the better efficiency of the new proposed structures. The photochemical mechanisms are studied by steady state photolysis, fluorescence, cyclic voltammetry, laser flash photolysis and electron spin resonance spin-trapping techniques.

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## 1. Introduction

Diketopyrrolopyrrole (DPP) derivatives have found various applications in dye-sensitized solar cells (DSSCs), organic photovoltaic cells (OPVs), field effect transistors (FETs), chemical sensors, inks, paints and plastics due to their unique  $\pi$ -conjugated structures and exceptional stability. Recent reviews on the use of DPP in these fields are given in Refs. [1–3]. As a consequence of the uniquely planar conjugated bicyclic structure and electron-withdrawing property of the DPP skeleton, the thiophene moiety Th containing derivatives can exhibit a band-shift to the longer wavelength absorption through an intramolecular charge transfer from the thiophene unit to the DPP core [4,5].

In a recent paper [6], a DPP-Th derivative has been used, for the first time to the best of our knowledge, in photoinitiating systems PISs under green light irradiation in polymerization reactions. In the present work, we propose a second generation of DPP-furan derivative **FuDPP** and other related compounds (Scheme 1) as photoinitiators (PI) for the cationic polymerization (CP)/free radical promoted

cationic polymerization (FRPCP) of epoxides or the free radical polymerization (FRP) of acrylates under exposure to a soft halogen lamp as well as laser diodes at 473 nm (blue light) and 532 nm (green light). The photoinitiating abilities of these PISs (PI in combination with a diphenyliodonium salt Iod or an Iod/N-vinyl carbazole NVK mixture) will be studied. The photochemical mechanisms involved in the initiation species formation will be investigated by steady state photolysis, fluorescence, cyclic voltammetry, laser flash photolysis and electron spin resonance spin-trapping techniques. Structure/reactivity/efficiency relationships in these DPP based photoinitiating systems will be derived. Remarkably, some of these systems are characterized by a higher efficiency than references based on camphorquinone, a well known photosensitizer for visible light.

## 2. Experimental

### 2.1. Materials

The chemical structures of the monomeric diketopyrrolopyrrole-furan derivative 2,5-bis(2-octyldodecyl)-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**FuDPP**) and the corresponding copolymer noted **PDBFBT** in [8], the benzodipyrrolinone derivative 3,7-bis(4-bromophenyl)-1,5-bis(2-decyltetradecyl)pyrrolo[2,3-f]

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indole-2,6(1*H*,5*H*)-dione (**M2**) and the corresponding copolymer noted **P2** in [9], and other studied compounds are shown in Schemes 1 and 2. These structures (**FuDPP** [7,8], **M2** [9], **PDBFBT** (the number average molecular weight  $M_n = 35.2$  kDa and the polydispersity index PDI = 2.60 relative to polystyrene) [8] and **P2** ( $M_n = 19.8$  kDa, PDI = 1.78 relative to polystyrene) [9]) were synthesized according to previously reported procedures.

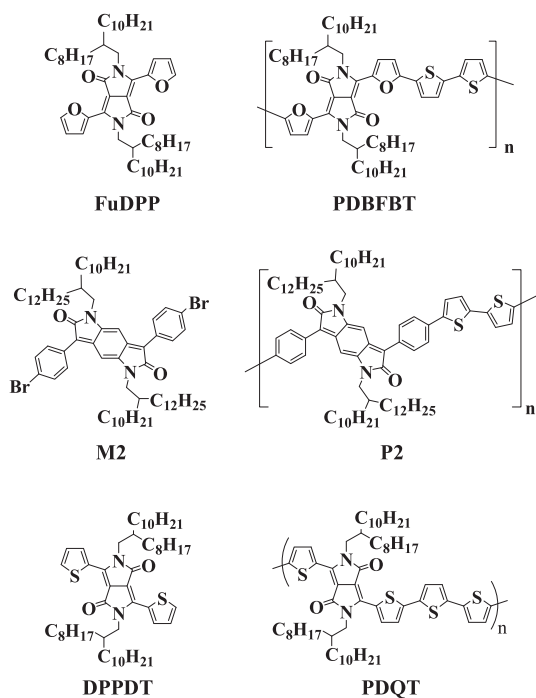
Camphorquinone (CQ), diphenyliodonium hexafluorophosphate (Iod), *N*-vinylcarbazole (NVK), methyl diethanolamine (MDEA), phenacyl bromide (R-Br) and the other reagents and solvents were purchased from Sigma–Aldrich or Alfa Aesar and used as received without further purification. (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX) and trimethylolpropane triacrylate (TMPTA) were obtained from Cytec and used as benchmark monomers to characterize the polymerization ability of the photoinitiating systems.

## 2.2. Computational procedure

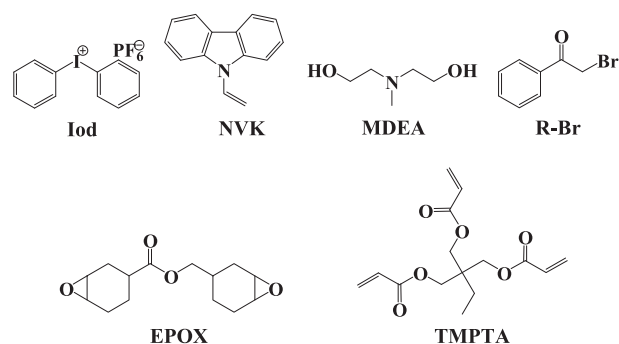
Molecular orbital calculations were carried out with the Gaussian 03 package. The electronic absorption spectra for the different compounds were calculated with the time-dependent density functional theory at B3LYP/6-31G\* level on the relaxed geometries calculated at UB3LYP/6-31G\* level; the molecular orbitals involved in these transition can be extracted [10,11]. The geometries were frequency checked.

## 2.3. Irradiation sources

Different irradiation sources were used for the photopolymerization experiments: polychromatic light from a halogen lamp (Fiber-Lite, DC-950; incident light intensity:  $I_0 \approx 12$  mW cm<sup>-2</sup> in the 370–800 nm range; the emission spectrum is given in SI) and laser diodes at 457 nm (~100 mW cm<sup>-2</sup>), 473 nm (~100 mW cm<sup>-2</sup>), 532 nm (~100 mW cm<sup>-2</sup>), 635 nm (~100 mW cm<sup>-2</sup>) and 808 nm (~500 mW cm<sup>-2</sup>).



**Scheme 1.** Chemical structures of the monomeric and polymeric photoinitiators (**FuDPP**, **M2**, **PDBFBT** and **P2**) used in this study and the previously investigated dyes (**DPPDT** and **PDQT**) [6].



**Scheme 2.** Chemical structures of the additives and the monomers.

## 2.4. Photopolymerization experiments

The experimental conditions of the photopolymerization reactions are given in the caption of Figs. 3 and 4. The photosensitive formulations were deposited on a BaF<sub>2</sub> pellet in air or in laminate (25 μm thick) for irradiation with different lights. The epoxy group content of EPOX and the double bond content of TMPTA were continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) [12,13] at 790 cm<sup>-1</sup> and 1630 cm<sup>-1</sup>, respectively.

## 2.5. Fluorescence measurements

The fluorescence properties of **FuDPP** were studied using a JASCO FP-750 spectrometer. The interaction rate constant  $k_q$  between **FuDPP** and Iod was extracted by classical Stern–Volmer treatments [14] ( $I_0/I = 1 + k_q\tau_0$  [Iod], where  $I_0$  and  $I$  stand for the fluorescent intensity of **FuDPP** in the absence and the presence of the Iod quencher, respectively, and  $\tau_0$  stands for the lifetime of the **FuDPP** excited singlet state in the absence of Iod). The fluorescence quantum yield of **FuDPP** was determined using anthracene as a reference.

## 2.6. Redox potentials

The oxidation potential ( $E_{ox}$  vs. SCE) of **FuDPP** was measured in acetonitrile/toluene (50%/50%, V/V) by cyclic voltammetry with tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte (Voltalab 6 Radiometer). The working electrode was a platinum disk and the reference electrode was a saturated calomel electrode (SCE). Ferrocene was used as a standard, and the potentials determined from the half peak potential were referred to the reversible formal potential of this compound (+0.44 V/SCE). The free energy change  $\Delta G$  for an electron transfer between **FuDPP** and Iod was calculated from the classical Rehm–Weller equation (eq. (1)), where  $E_{ox}$ ,  $E_{red}$ ,  $E_S$  (or  $E_T$ ) and  $C$  are the oxidation potential of **FuDPP**, the reduction potential of Iod, the excited singlet (or triplet) state energy of **FuDPP** and the electrostatic interaction energy for the initially formed ion pair, generally considered as negligible in polar solvents) [15]:

$$\Delta G = E_{ox} - E_{red} - E_S \text{ (or } E_T) + C \quad (1)$$

## 2.7. Laser flash photolysis

Nanosecond laser flash photolysis (LFP) experiments were carried out using a Q-switched nanosecond Nd/YAG laser ( $\lambda_{exc} = 355$  nm, 9 ns pulses; energy reduced down to 10 mJ) from

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