Polymeric Photoinitiators: A New Search toward High Performance Visible Light Photoinitiating Systems

Jing Zhang, Pu Xiao, Frédéric Dumur,* Chang Guo, Wei Hong, Yuning Li, Didier Gigmes, Bernadette Graff, Jean-Pierre Fouassier, Jacques Lalevée*

A series of conjugated polymers and oligomers previously used in organic photovoltaics and organic light-emitting diodes (OLEDs) have been examined for the first time as photoinitiators of polymerization. They address the present and future challenges facing photopolymerization: requirement of high extinction molar coefficients, absorption over the whole visible spectrum, ability to easily withdraw or release electrons. Interestingly, these compounds initiate the cationic polymerization of epoxides or the free radical polymerization of acrylates upon exposure of the photoinitable formulations to a LED emitting at 405 nm. Some of them can potentially operate under blue, green, or red laser diodes.

1. Introduction

During the past decade, the photopolymerization area has witnessed intense research efforts due to the constant growth of industrial applications. Notably, applications of photopolymers range from conventional areas such as coatings, inks, and adhesives to high-tech domains, e.g., optoelectronics, laser imaging, stereolithography, 3D-printing, or nanotechnology.[1] A light induced polymerization reaction requires the presence of a molecule, usually denoted as a photoinitiator (PI) (although it could sometimes exhibit a behavior of photosensitizer or photocatalyst) and having a strong absorption in the required wavelength range, which is incorporated into a photoinitiating system (PIS).[2] Recently, a major breakthrough has been achieved in the field of PI operating under visible lights and low light intensity sources, providing a revival of interest for this polymerization technique known since decades.[3]

Presently, the search for new dyes acting as PIs (exhibiting high molar extinction coefficients and visible light absorption spectra) together with suitable designed PISs still remains an active research field facing the fact that all historical UV-operating PIs such as benzophenones, thioxanthenes, or benzoin ethers can be clearly discarded for this purpose due to the lack of a sufficient absorption beyond 400 nm. If derivatives of these benchmark PIs and others PIs (e.g., camphorquinone, bis phosphine oxides, some dyes) have been proposed over the years, the chemical engineering required to develop novel...
structures remains a hard work (see recent references, e.g., in refs. [4] and [5]). Clearly, new innovative structures exhibiting naturally a strong absorption in the visible region have to be researched and tested in photopolymerization reactions. With regards to the potential applications of photopolymers, a second topic of current interest concerns the extractability of the residues issued from polymerization (unreacted PIs, side-products issued from the polymerization reactions). If a few examples of low-molecular weight PIs bearing a co-polymerizable moiety (e.g., acrylate group) have recently been proposed, the low migration can also be ensured by means of PIs exhibiting a high molecular weight. This strategy is particularly efficient with polymeric PIs for which the intimate interplay of the resulting polymer chains ensures a definitive immobilization of the PI into the polymer network.

In this paper, a series of new dyes developed for organic electronics and still not investigated as PIs yet are proposed (Scheme 1) and tested for the first time in the photopolymerization of acrylates and epoxides upon light emitting diode (LEDs) irradiations. Notably, poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl-alt-(1,3-(5-octyl-4H-thieno[3,4-c]pyrrole-4,6-(5H)-dione))] (PBDTBO-TPDO) stands out as electron-donating co-polymers of high interest for polymer solar cells. PTB7 is an electron-donating semi-conducting co-polymer often associated with poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene-2,6-diyl]] (PCPDTBT) in ternary solar cells whereby PTB7 (which exhibits a low energy bandgap, \( E_g = 1.6 \) eV) (the energy band gap is a good indicator of the visible light absorption properties) is added in complement of PCPDTBT \( (E_g = 1.8 \) eV).[10] In parallel, PCDTBT is one of the latest generation of conjugated polymers that have been designed for organic photovoltaics (OPV) applications.[11] High power conversion efficiencies were also reported with PBDTBO-TPDO \( (E_g = 1.73 \) eV) characterized by a \( \pi \)-conjugated backbone structure and designed with a linear alkyl substituent appended to \( N \)-alkylthieno[3,4-c]pyrrole-4,6-dione to provide a planarization of the conjugated backbone.[9] Conversely, DTS(FBTh\(_2\)) \( (E_g = 1.78 \) eV) is not a conjugated polymer but a small-molecule donor compound. Apart from this important

![Scheme 1. The different compounds investigated in this study.](image-url)
reacts with Iod and generates a dye cation radical (Dye$^+$). The corresponding PISs (NVK) for the development of new high performance photoinitiating systems (PISs) or Dye/Iod/NVK systems have been examined as PIs due to the similarity of their absorption spectra with those of the aforementioned compounds. For comparison, IDG1 previously used in photopolymerization[14] has been also revisited in this study.

All these dyes will be mixed either with diphenyliodonium hexafluorophosphate (Iod) and N-vinylcarbazole (NVK) for the development of new high performance photoinitiating systems (PISs). The corresponding PISs operate as observed in other Dye/Iod or Dye/Iod/NVK systems already described by us. Briefly (Scheme 2), the dye reacts with Iod and generates a dye cation radical (Dye$^+$) and a phenyl radical (Ph$^•$). This radical adds to the NVK double bond and forms a Ph-NVK$^-$ radical. Both radicals initiate a free radical polymerization (FRP). The produced Ph-NVK$^-$ radical is oxidized by Iod to form a Ph-NVK$^+$ cation suitable for a free radical promoted cationic polymerization (FRPCP). The cationic polymerization (CP) is initiated by Dye$^{•+}$.

The polymerization initiating ability of all these Dye/Iod and Dye/Iod/NVK PISs will be checked by real-time Fourier transform infrared (FTIR) spectroscopy. FRP, CP, and FRPCP will be conducted under exposure to a LED emitting at 405 nm so that the relative efficiencies can be easily evaluated.

2. Experimental Section

2.1. The Compounds Used as PIs

The different compounds investigated in this study are presented in the Scheme 1. Poly[4,8-bis-(2-ethylhexyloxyl)benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl][3-fluoro-2-(2-ethylhexyloxyl)carbonyl][thieno[3,4-b]thiophenediyl][PTB7, poly[N-9’-heptadecanyl-2,7-carbazole-alt-5,5-((4’,7’-di-2-thienyl-2,1,3-benzothiadiazole) PCDTBT, 7,7’-bis-(2-ethylhexyloxyl)-4H-silole-[3,2-b:4,5-b’]dithiophene-2,6-diyl]bis(6-fluoro-4-(5’-hexyl-2,2’-bithiophen)-5-yl)benzoc[1]h[2,5]thiadiazole] DTS(FBTTh$_2$)$_2$, and poly[4,8-bis-(2-ethylhexyloxyl)benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl-alt-(1,3-(5-octyl-4-fluoro-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione))] PBDTBO-TPDO were purchased from Lumtec, whereas poly[[9,9-diocyl-2,7-divinylene-fluorenylene]alt-co-[2-methoxy-5-(2-ethyl-hexyloxyl)-1,4-phenylene]] ADS109GE was supplied from American Dye Source, Inc. All dyes were used with the highest purity available. IDG1 and IDG2 (Supporting Information) were synthesized as previously reported.[16] Synthesis of PBBTZ20 was described in Supporting Information.

2.2. Other Chemical Compounds

Iod and NVK (Scheme 3) were purchased from Sigma-Aldrich and used as received without further purification. Trimethylolpropane triacrylate (TMPTA) and (3,4-epoxy-cyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX) were obtained from Allnex and used as benchmark monomers for radical and cationic photopolymerization reactions.

2.3. Irradiation Sources

A LED at 405 nm (M405L2 – ThorLabs; ≈110 mW cm$^{-2}$) was used for the irradiation of the photocurable samples.

2.4. Computational Procedure

Molecular orbital calculations were carried out with the Gaussian 03 package. The electronic absorption spectra for the FM derivatives were calculated from the time-dependent density functional theory at B3LYP/6-31G* level on the relaxed geometries of these last level; the molecular orbitals involved in these electronic transitions were also extracted.

2.5. Photopolymerization Experiments

For photopolymerization experiments, the conditions are given in the figure captions. The photosensitive formulations (25 μm thick) were deposited on a BaF$_2$ pellet in laminate (the
formulation is sandwiched between two polypropylene films to avoid the re-oxygenation during the photo-polymerization or under air and irradiated with different light sources. The evolution of the TMPTA double bond content or the EPOX epoxy group content were continuously followed by real time FTIR spectroscopy (JASCO FTIR 4100) at about 1630 and 790 cm⁻¹, respectively \[27\]. TMPTA and EPOX being multifunctional mono- mers, the conversion indicated in the present paper correspond to the conversion in the polymerizable functions (acrylate and epoxy functions, respectively).

2.6. Redox Potentials

The oxidation potentials (\(E_{ox}\) vs standard calomel electrode (SCE)) of the investigated compounds used as PIs were measured in acetonitrile by cyclic voltammetry with tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte (Voltalab 6 Radiometer). The procedure has been presented in detail in ref.\[27\]. The free energy change \(\Delta G_{et}\) of the electron transfer reaction between \(1^\text{PIs}\) and Iod can be calculated from the classical Rehm–Weller equation: \[\Delta G_{et} = E_{red} - E_{ox} - E_1 (or E_2) + C; \text{ where } E_{red}, E_{ox}, E_1 \; (or \; E_2), \text{ and } C \; \text{are the oxidation potential of the studied photoinitiators, the reduction potential of iod, the excited singlet state energy of the studied PIs, and the electrostatic interaction energy for the initially formed ion pair (this latter parameter is generally considered as negligible in polar solvents).}\[18\]

3. Results and Discussion

3.1. Absorption Properties of the New Dyes

The ground state absorption spectra of the new proposed dyes are depicted in Figure 1 and the relevant photophysical characteristics of the different compounds are gathered in Table 1. The absorption maxima \(\lambda_{max}\) are located at 671, 554, 580, 589, and 481 nm for PTB7, PCDTBT, DTS(FBTTh)₂, PBDBO-TPDO, and ADS109GE, respectively. Considering their initial use as chromophores for solar cells, the different dyes exhibit absorption spectra largely covering the visible range (see Figure 1). Notable, PTB7, PCDTBT, PBDBO-TPDO, and DTS(FBTTh)₂ share in common thiophene units as electron-donating groups, ensuring low oxidation potentials. On the opposite, the low band gap polymer ADS109GE is characterized by two electron-donating units (fluorene and dialkoxybenzene) connected to the accepting cyano groups. Due to the weak electron-accepting ability of this group, the absorption spectrum of the light-emitting polymer is less extended than those observed for the materials devoted to photovoltaics applications and only ranges in the 350–550 nm region. Still based on push–pull structures, IDG1, IDG2, and PBDBTZ20 are respectively based on the indigo and the 5H-pyrrolo-bis-thiazine scaffolds. Absorption maxima corresponding to the positions of the intramolecular charge transfer band are respectively determined at 591, 540, and 450/480 nm for IDG1, IDG2, and PBDBTZ20. Interestingly, most of the compounds examined in this study are soluble in common organic solvents: this is directly related to the primary use of these materials, i.e., the optoelectronic devices (OLEDs, solar cells, transistors) by solution process. From this specificity, a sufficient solubility of the dyes in the different envisioned formulations is observed, except for PTB7 and PBDBO-TPDO that are insoluble in EPOX and TMPTA. Beyond the solubility, all dyes, thanks to their absorption spectra clearly centered in the visible range, are suitable for irradiations with LED bulbs emitting at 405 nm and other devices such as laser diodes emitting at 457 and 532 nm and even in the red.

The molecular orbitals (MO) involved in the lowest HOMO → LUMO energy transition (where HOMO and LUMO stand for the highest occupied and lowest unoccupied molecular orbitals, respectively) are depicted in Figure 2. The calculations were restricted to a single monomer unit to reduce the computational cost. As anticipated, all dyes (PTB7, PCDTBT, PBDBO-TPDO, DTS(FBTTh)₂) possessing thiophene units as electron-donating groups showed a HOMO level centered on this group, the LUMO level being located on the electron-accepting part. Due to the presence of a HOMO and a LUMO level spatially well-separated on these compounds, a clear distinction between the electron withdrawing and electron-releasing part can be established. On the opposite, for the four other dyes (ADS109GE, IDG1, IDG2, and PBDBTZ20) exhibiting weak electron donor and acceptor properties, this separation could not be detected and a contribution of the whole molecule to the two orbitals could be evidenced. Theoretical investigation of their respective HOMO and LUMO energy values revealed these latter to be highly dependent of the co-monomers used. Differences of reactivity can already be anticipated for these photoinitiators.

![Figure 1. Normalized UV-visible absorption spectra of the different dyes in THF (except for IDG2 in acetonitrile).](image)
### Table 1. Ground state absorption maxima (nm).

<table>
<thead>
<tr>
<th>Dyes</th>
<th>$\lambda_{\text{max}}$ (Abs) [nm]</th>
<th>$E_{\text{HOMO}}$ [eV]</th>
<th>$E_{\text{LUMO}}$ [eV]</th>
<th>$E_{\text{HOMO}}$ [eV]</th>
<th>$E_{\text{LUMO}}$ [eV]</th>
<th>$E_{\text{ox}}$ [V vs SCE]</th>
<th>$\Delta G$ [eV] (dye/Iod)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7</td>
<td>622, 671</td>
<td>$-5.15^{[20]}$</td>
<td>$-3.31^{[20]}$</td>
<td>$-5.25$</td>
<td>$-2.18$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCDTBT</td>
<td>391, 554</td>
<td>$-5.45^{[21]}$</td>
<td>$-3.60^{[22]}$</td>
<td>$-4.90$</td>
<td>$-2.61$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DTS(FBTTh$_2$)$_2$</td>
<td>372, 580</td>
<td>$-5.12^{[23]}$</td>
<td>$-3.34^{[23]}$</td>
<td>$-4.65$</td>
<td>$-2.78$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBDTBO-TPDO</td>
<td>408, 589</td>
<td>$-5.40^{[9]}$</td>
<td>$-5.33$</td>
<td>$-2.20$</td>
<td>$0.88^{[9]}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ADS109GE</td>
<td>455, 481</td>
<td>–</td>
<td>–</td>
<td>$-5.52$</td>
<td>$-2.01$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IDG1</td>
<td>548 (s), 591</td>
<td>–</td>
<td>–</td>
<td>$-6.10$</td>
<td>$-3.16$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IDG2</td>
<td>500 (s), 540</td>
<td>–</td>
<td>–</td>
<td>$-6.04$</td>
<td>$-2.94$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBBTZ20</td>
<td>450, 480</td>
<td>–</td>
<td>–</td>
<td>$-4.98$</td>
<td>$-2.10$</td>
<td>$1.25$</td>
<td>$-1.09$</td>
</tr>
</tbody>
</table>

$^{a)}$Energy levels reported in the literature; $^{b)}$Energy levels determined by theoretical calculations; $^{c)}$Oxidation potential determined experimentally; $^{d)}$The free energy change $\Delta G$, calculated from the classical Rehm–Weller equation:

$$\Delta G = E_{\text{ox}} - E_{\text{red}} - E_{S} \text{ (or } E_{T} \text{) } + C;$$

where $E_{\text{ox}}, E_{\text{red}}, E_{S} \text{ (or } E_{T} \text{)},$ and $C$ are the oxidation potential of the studied photoinitiators, the reduction potential of Iod, the excited singlet (or triplet) state energy of the studied photoinitiators, and the electrostatic interaction energy for the initially formed ion pair. This latter parameter is generally considered as negligible in polar solvents.

### Figure 2. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the different dyes at UB3LYP/6-31G* level; for the MO calculations, an ethyl group instead of the alkyl chain was considered for IDG1 and a propyl group instead of the alkyl chain for PCDTBT, PBBTZ20, and PBDTBO-TPDO.
3.2. Cationic Photopolymerization of Epoxides

The cationic photopolymerization of EPOX was carried out under air upon exposure of the different dyes/Iod combinations to a low consumption LED emitting at 405 nm (≈110 mW cm\(^{-2}\)) (see Figures 3–6). As evidenced in Figure 3, in the presence of PCDTBT/Iod or DTS(FBTTh\(_2\))\(_2\)/Iod, a moderate final conversion (FC) of 20% was obtained with PCDTBT/Iod after 800 s of irradiation with the LED@405 nm (see Table 2); no polymerization occurred with DTS(FBTTh\(_2\))\(_2\)/Iod as likely resulting from its insolubility in EPOX. While adding NVK, comparable FCs were obtained: FCs = 46 and 49% using PCDTBT/Iod/NVK and DTS(FBTTh\(_2\))\(_2\)/Iod/NVK, respectively. The polymerization ability of DTS(FBTTh\(_2\))\(_2\)/Iod/NVK can be confidently assigned to an improved solubility of the dye in the formulation, resulting from the presence of NVK.

Considering that ADS109GE does not exhibit a sufficient absorption at 405 nm, the cationic polymerization of EPOX was carried out upon irradiation with the LED@455 nm (M455L3 – ThorLabs; ≈80 mW cm\(^{-2}\)) or the halogen lamp (intensity = 12 mW cm\(^{-2}\)). Good polymerization profiles were obtained upon the halogen lamp exposure (e.g., FC = 29 and 36% respectively after 800 s of irradiation using ADS109GE/Iod and ADS109GE/Iod/NVK, respectively (see Figure 4). On the opposite, only a low final conversion (FC ≈ 16%) was obtained upon the LED@455 nm exposure, these counter-performances being directly related to the lower light intensity of the LED bulb compared to the halogen lamp.

From the series of dyes investigated in this study, PBBTZ20/Iod/NVK led to the best polymerization profiles, with FC = 58% after 800 s of irradiation (LED@405 nm; see Figure 5). A comparison established with the previously reported IDG1/Iod/NVK\(^{[16]}\) evidenced that PBBTZ20 outperformed IDG1 (FC = 52% in the same experimental conditions). The high FCs are in line with the good absorption of PBBTZ20 at 405 nm.

In the IDG1 and IDG2 indigo derivatives, the chromophores possess the same central core but differ by the length of the alkyl chains. As shown in Figure 6, the new IDG2/Iod/NVK system led to a final reduced conversion of ≈30% compared to IDG1/Iod/NVK. Considering that the two dyes exhibit the same scaffold, the lower performance of IDG2 can be assigned to the lower solubility resulting from the presence of shorter alkyl chains. Once again, the practical photoinitiating ability of a molecule is intimately linked to its solubility in the photocurable formulation.
3.3. Free Radical Photopolymerization of Acrylates

In light of the above results and its remarkable photoinitiating ability, only PBBTZ20 was selected for the radical polymerization of a trifunctional acrylate monomer (TMPTA) at 405 nm (see Figure 7 and Table 3). A final conversion of 32% was achieved with PBBTZ20/Iod/NVK (Figure 7 curve 1) versus FC = 42% with IDG1/Iod/NVK (Figure 7, curve 2). The IDG1/MEDA/R-Cl three-component system (that works through a reduction cycle as in ref. [1]) led to a less efficient polymerization profile (FC = 37% after 400 s).

4. Conclusions

Seven new dyes have been examined as photoinitiators for the polymerization of acrylate and/or epoxide monomers. Among all chromophores, PBBTZ20/Iod/NVK proved to be the most efficient for the cationic polymerization of epoxides. Indeed, especially, for the polymerization of EPOX, this 5H-pyrrolo-bis-thiazine derivative could outperform the IDG1/Iod/NVK reference system which is already better than similar Eosin or camphorquinone based combinations. PBBTZ20 belongs to an unknown class of photoinitiators so far and the preliminary results presented in this work make this new family a promising scaffold for future developments. For radical polymerization, IDG1 is found a good photoinitiator. Most of the experimental work has been carried out here on the ability of the Dye/Iod/NVK systems to work at 405 nm where their relative efficiency can be evaluated. The excited state reactivity being not wavelength dependent in such systems (as observed with many other similar PISs), it is obvious that an efficient

Table 2. EPOX conversions obtained under air upon exposure to the LED@405 nm for 800 s in the presence of Dye/Iod (0.5%/2%, w/w) or Dye/Iod/NVK (0.5%/2%/3%, w/w/w).

<table>
<thead>
<tr>
<th>LED (405 nm)</th>
<th>PCDTBT/Iod</th>
<th>DTS(FBTTb2)2/Iod</th>
<th>DTS(FBTTb2)2/Iod/NVK</th>
<th>ADS109GE/Iod</th>
<th>ADS109GE/Iod/NVK</th>
<th>IDG1/Iod</th>
<th>IDG1/Iod/NVK</th>
<th>IDG2/Iod</th>
<th>IDG2/Iod/NVK</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCDTBT/Iod</td>
<td>20%</td>
<td>np</td>
<td>np</td>
<td>–</td>
<td>–</td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>np</td>
</tr>
<tr>
<td>PCDTBT/Iod/NVK</td>
<td>46%</td>
<td>np</td>
<td>np</td>
<td>–</td>
<td>–</td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>np</td>
</tr>
<tr>
<td>DTS(FBTTb2)2/Iod</td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>–</td>
<td>–</td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>np</td>
</tr>
<tr>
<td>DTS(FBTTb2)2/Iod/NVK</td>
<td>49%</td>
<td>np</td>
<td>np</td>
<td>–</td>
<td>–</td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>np</td>
</tr>
<tr>
<td>ADS109GE/Iod</td>
<td>–</td>
<td>np</td>
<td>np</td>
<td>–</td>
<td>–</td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>np</td>
</tr>
<tr>
<td>ADS109GE/Iod/NVK</td>
<td>–</td>
<td>np</td>
<td>np</td>
<td>–</td>
<td>–</td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>np</td>
</tr>
<tr>
<td>PBBTZ20/Iod</td>
<td>34%</td>
<td>np</td>
<td>np</td>
<td>–</td>
<td>–</td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>np</td>
</tr>
<tr>
<td>PBBTZ20/Iod/NVK</td>
<td>58%</td>
<td>np</td>
<td>np</td>
<td>–</td>
<td>–</td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>np</td>
</tr>
<tr>
<td>IDG1/Iod</td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>–</td>
<td>–</td>
<td>np</td>
<td>np</td>
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<td>np</td>
</tr>
<tr>
<td>IDG1/Iod/NVK</td>
<td>52%</td>
<td>np</td>
<td>np</td>
<td>–</td>
<td>–</td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>np</td>
</tr>
<tr>
<td>IDG2/Iod</td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>–</td>
<td>–</td>
<td>np</td>
<td>np</td>
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<td>np</td>
</tr>
<tr>
<td>IDG2/Iod/NVK</td>
<td>35%</td>
<td>np</td>
<td>np</td>
<td>–</td>
<td>–</td>
<td>np</td>
<td>np</td>
<td>np</td>
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</tr>
</tbody>
</table>

np = 17% using ADS109GE/Iod/NVK under the 457 nm laser diode exposure.

Table 3. TMPTA conversions obtained in laminate upon exposure to the LED@405 nm for 400 s in the presence of Dye/Iod (0.5%/2%, w/w) or Dye/Iod/NVK (0.5%/2%/3%, w/w/w).

<table>
<thead>
<tr>
<th>LED (405 nm)</th>
<th>PBBTZ20/Iod</th>
<th>PBBTZ20/Iod/NVK</th>
<th>IDG1/Iod</th>
<th>IDG1/Iod/NVK</th>
<th>IDG1/MDEA/R-Cl</th>
<th>IDG2/Iod</th>
<th>IDG2/Iod/NVK</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>&lt;10%</td>
<td>32%</td>
<td>np</td>
<td>42%</td>
<td>37%</td>
<td>–</td>
<td>–</td>
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<td></td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>np</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
system at 405 nm will remain efficient under exposure to other visible light sources providing a good matching with the absorption spectra: this is the case for, e.g., PBDTT20 at 470 nm, PCDTBT at 532 nm or DTS(FBTTh)$_2$ at 532 or 605 nm. If the examination of compounds developed for organic electronics is unusual for the polymer community and mostly developed by our research groups, it can offer the possibility to propose new highly reactive scaffolds.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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