



Near UV–vis LED-excitable two-branched sensitizers for cationic, radical, and thiol-ene photopolymerizations



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ABSTRACT

Two novel branched sensitizers bearing biphenyl or fluorenyl groups as the linking skeleton and triphenylamine-stilbene-thiomethyl benzonitrile as peripheral branches were designed. Strong absorption of light in the UV–vis range ($\lambda_{\max} = 389\text{--}397\text{ nm}$, $\epsilon_{\max} = 60,200\text{--}90,300\text{ M}^{-1}\text{ cm}^{-1}$) matched the emission of new light sources, i.e., UV–vis light-emitting diodes at 365–450 nm. The reactive species produced from the photoinitiating systems based on these chromophores themselves or combined with an iodonium salt, N-vinylcarbazole, or an amine were highly efficient for versatile photopolymerizations (radical, cationic, and thiol-ene polymerizations) upon soft exposure conditions (365–450 nm light-emitting diodes). The UV–vis spectra, theoretical calculation of molecular orbitals, electrochemistry, and fluorescence quenching measurements were studied to reveal the photochemical mechanism.

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1. Introduction

Photopolymerizations, which use photoinitiators (PIs) or photoinitiating systems (PISs) to initiate the chain reaction for forming polymer materials, have useful applications in radiation curing, photoimaging, optics, medicine, microelectronics, and nanotechnology [1–7]. Compared with thermal and redox polymerizations, the most important advantage of photopolymerization is that it can be controlled by manipulating the intensity and wavelength of the radiation sources [5]. Light-emitting diodes (LEDs) are novel light sources that have recently attracted increasing attention for photopolymerization applications because of their efficient light output and low cost [8–15]. However, most reported and commercial PIs exhibit less-than-perfect performance upon LED irradiation because they have a maximum absorbance below 365 nm where the most common and cost-effective UV/LED lamps irradiate [16].

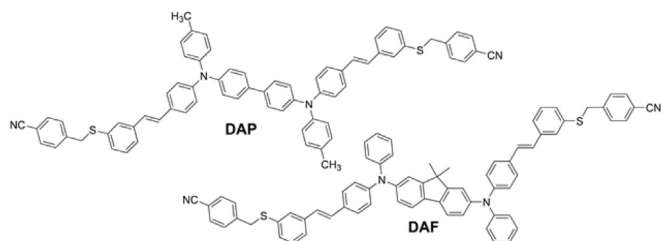
For photopolymerization, free radical polymerization (FRP) [17], cationic polymerization (CP) [18], interpenetrated polymer network (IPN) synthesis [19], and thiol-ene polymerization (TEP) [20] are known for the formation of highly cross-linked networks in

different photocuring fields [5]. Efficient versatile PIs are highly useful for photopolymerization reactions [21–24]. Many multi-component mixtures (PIs/coinitiators) are good versatile PISs, which perform a concomitant radical/cationic dual curing in a one step procedure upon excitation in the UV–visible range has been described in recent years [25–34]. In addition, polyazomethines and naphthoylenebenzimidazolone dyes [35–39] have also been used as initiators or sensitizers in free-radical/cationic hybrid photopolymerizations, and they are potential versatile PIs.

Therefore, the design and development of new versatile PIs with excellent photochemical properties matching the output wavelength of LEDs are an important research direction in photopolymerization. In the present paper, we design and develop two novel sensitizers, namely, 4,4'-di-(N-(4-(3-(4-cyanobenzylthio)styryl)phenyl)-N'-4-methylphenyl)aminobiphenyl (DAP, Scheme 1) and 2,7-di-(N-(4-(3-(4-cyanobenzylthio)styryl)phenyl)-N'-phenyl)amino-9,9'-dimethyl-9H-fluorene (DAF, Scheme 1) with symmetric two-branched structures. In the structures of DAP and DAF, biphenyl and fluorene units exhibit twisted or planar geometry where a strong electron delocalization is expected, and the absorption of PIs is prolonged to 350–450 nm. Their roles as near UV–vis LED-excitable versatile PIs based on these dyes themselves or combined with an iodonium salt, N-vinylcarbazole, or an amine for FRP, CP, and TEP will be studied by real-time Fourier transform infrared (FT-IR) spectroscopy. The production of reactive species

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Scheme 1. Molecular structures of the two sensitizers.

(radicals and cations) from the PIs in the absence or presence of iodonium salt, amine, and optional N-vinylcarbazole will be investigated by theoretical calculation, steady-state photolysis, fluorescence, and cyclic voltammetry techniques [37,40–42].

2. Experimental section

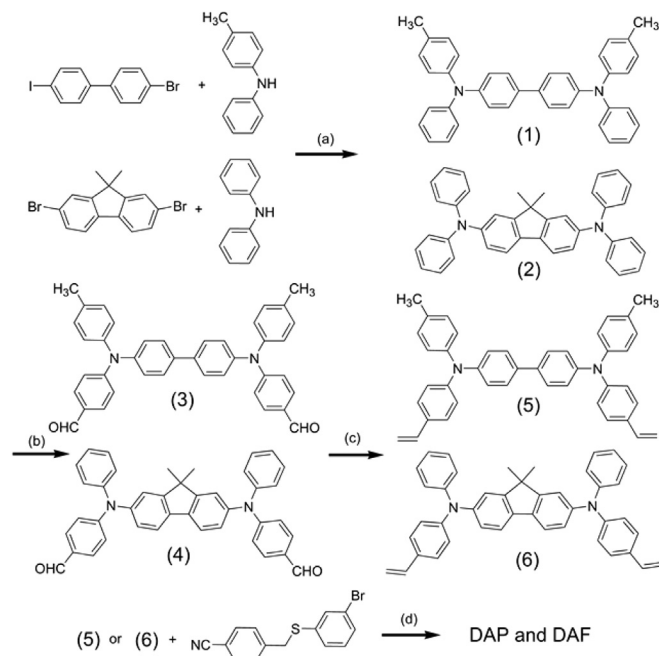
2.1. General

All synthesis reagents are purchased from Energy Company (Shanghai, China). Diphenyliodonium hexafluorophosphate (Iod), N-vinylcarbazole (NVK), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (EPOX), tri(ethylene glycol) divinyl ether (DVE-3), cyclohexene oxide (CHO), trimethylolpropane tris(3-mercaptopropionate) (Trithiol) and trimethylolpropane triacrylate (TMPTA) are supplied by J&K Chemicals (Scheme 2). The starting materials, 4-methyl diphenylamine, 4-bromo-4'-iodobiphenyl, diphenylamine, and 2,7-dibromo-9,9-dimethyl-9H-fluorene are supplied by J&K Chemicals (analytical reagent) and all the solvents employed are J&K Chemicals spectroscopic grade. Proton and carbon nuclear magnetic resonance spectra (^1H , ^{13}C NMR) are recorded on a Bruker Avance 500 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from the Me_4Si resonance which is used as the internal standard when recording NMR spectra. Element analysis was performed by Elementar Vario El III (Germany). Mass spectra were recorded on a Micromass GCTM (Scheme 3).

2.2. Synthesis

2.2.1. Synthesis of 4,4'-bis(N-phenyl-N'-(4-methylphenyl)aminobiphenyl (1)

4-Methyl diphenylamine (20.29 g, 0.11 mol) and 4-bromo-4'-iodobiphenyl (18.05 g, 0.05 mol) were added into the mixture of copper bronze (1.30 g, 0.02 mol), potassium carbonate (20.78 g,

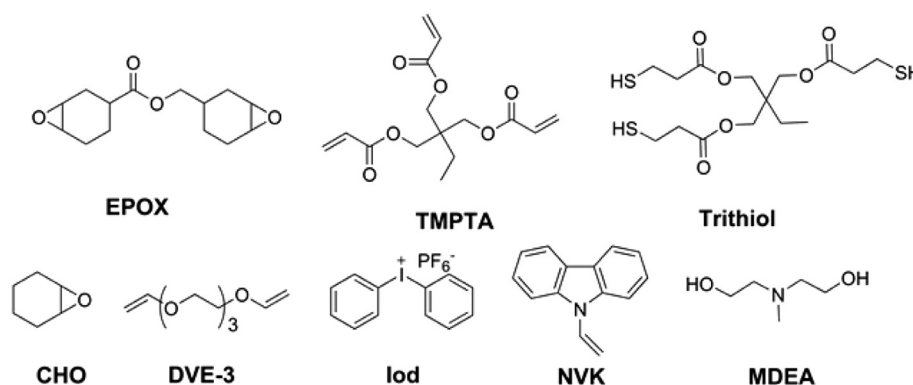


Scheme 3. Synthetic route of the PIs. a) Cu, K_2CO_3 , N_2 , 200 °C, 70 h, 1,2-dichlorobenzene; b) POCl_3 , DMF, 80 °C, 12 h, CHCl_3 ; c) MePh_3PBr , t-BuOK, N_2 , rt, 4 h, THF; d) Tri-*o*-tolylphosphine, $\text{Pd}(\text{OAc})_2$, TEA, DMF, N_2 , 110 °C, 48 h.

0.15 mol), and 18-crown-6 (1.16 g, 0.004 mol) in 1,2-dichlorobenzene (40 mL). The mixture was stirred under an inert atmosphere at 200 °C for 70 h. After cooling to room temperature the resulting mixture was extracted with dichloromethane and dried with Na_2SO_4 . After vacuum vaporation of 1,2-dichlorobenzene, the product was purified by column chromatography (silica gel, dichloromethane/petroleum ether, 1/15, v/v) to obtain white powder in 50% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.42 (d, J = 8.3 Hz, 4H, Ph), 7.27–7.19 (d, 4H, Ph), 7.09 (m, 12H, Ph), 7.04 (d, J = 8.2 Hz, 4H, Ph), 6.98 (t, J = 7.3 Hz, 2H, Ph), 2.32 (s, 6H, CH_3).

2.2.2. Synthesis of 4,4'-bis(N-(4-formyl)phenyl-N'-(4-methylphenyl)aminobiphenyl (3)

POCl_3 (3.2 mL, 0.03 mol) was added dropwise into DMF (3 mL, 0.04 mol) and the mixture was stirred under an inert atmosphere at 0 °C for an hour. Then, compound (1) (5.16 g, 0.01 mol) in CHCl_3 (30 mL) was added into the mixture, followed by stirring under an inert atmosphere at 80 °C overnight. After cooling to room



Scheme 2. Chemical structures of the monomers and additives.

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