Supporting Information

A Monocomponent Bifunctional Benzophenone-Carbazole Type II Photoinitiator for LED Photoinitiating Systems

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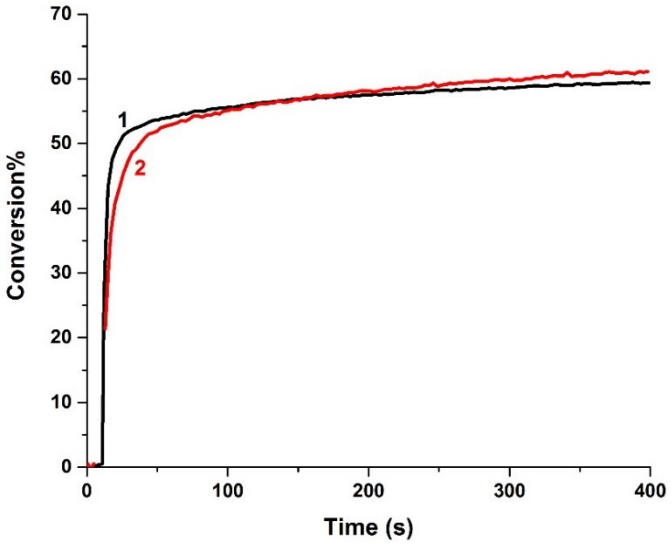


Figure S1. Photopolymerization profiles of TMPTA (acrylate function conversion vs. time) in laminate upon LED@365 nm irradiation in the presence of (1) ITX/EDB (0.3%/1%, mol/mol), (2) BPC/EDB (0.3%/1%, mol/mol). The irradiation starts from t = 10 s.

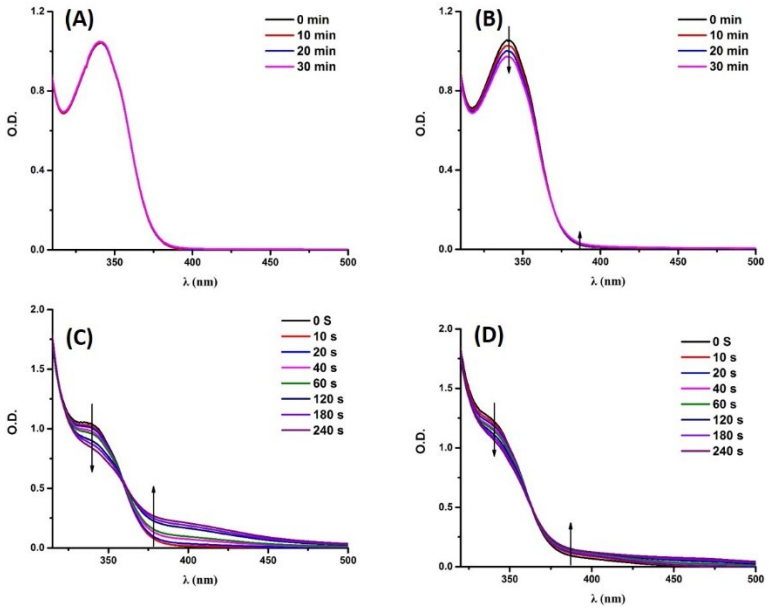


Figure S2. Photolysis of (A) BPC alone, (B) BPC/TEOA, (C) BPC/Iod, (D) BPC/TEOA/Iod upon LED@375 nm irradiation in acetonitrile ([Iod]=0.01M, [TEOA]=0.01M).

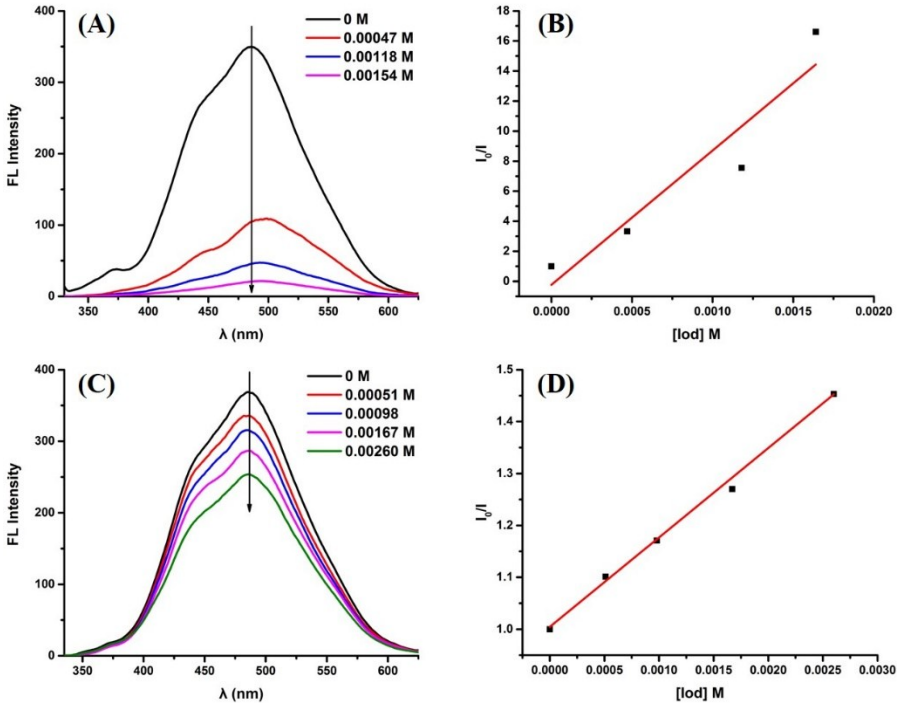


Figure S3. (A) Fluorescence quenching of BPC by EDB in acetonitrile, (B) Stern–Volmer treatment for BPC/EDB fluorescence quenching, (C) Fluorescence quenching of BPC by Iod in acetonitrile, (D) Stern–Volmer treatment for BPC/Iod fluorescence quenching.

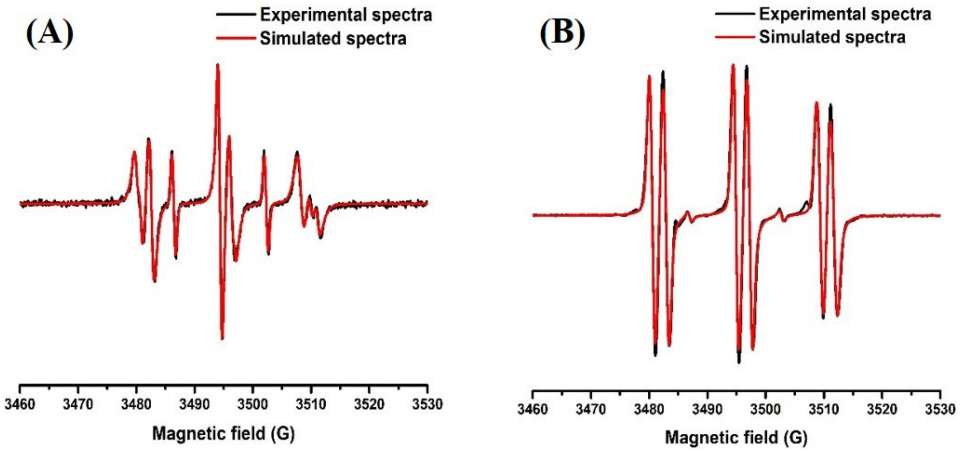


Figure S4. ESR-ST spectra of the radical adducts obtained in the presence of (A) BPC alone and (B) BPC/EDB/Iod upon LED@375 nm irradiation in tert-butylbenzene.

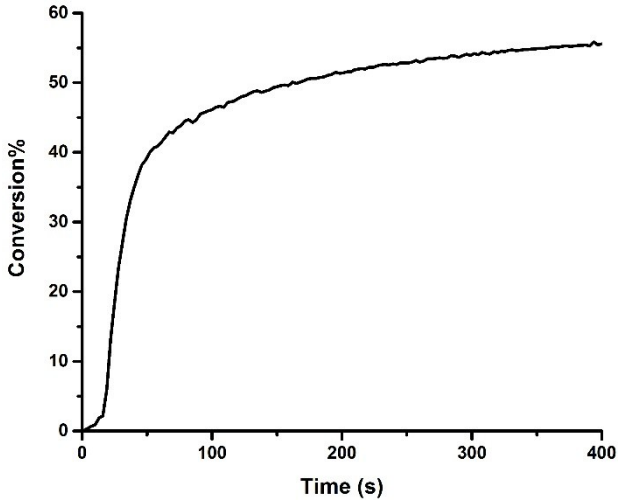


Figure S5. Photopolymerization profiles of TMPTA (acrylate function conversion vs irradiation time) in laminate upon LED@405 nm irradiation in the presence of BPC/EDB/Iod (0.5%/1%/1%, w/w/w). The irradiation starts from t = 10 s.

Table S1. Final acrylate function conversions for TMPTA and epoxy function conversion for EPOX upon LED@365 nm irradiation at t = 400 s.

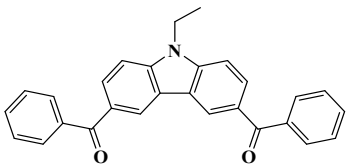
PISs	Conversion%

BPC - TMPTA	65
BPC/EDB-TMPTA	60
BPC/Iod-TMPTA	63
BPC/EDB/Iod-TMPTA	65
BP-TMPTA	0
BP/EDB-TMPTA	30
BPC/Iod-EPOX	46

Synthesis of BPC:

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. ^{1}H and ^{13}C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ^{1}H (400 MHz) and ^{13}C (100 MHz). The ^{1}H chemical shifts were referenced to the solvent peaks $CDCl_3$ (7.26 ppm) and the ^{13}C chemical shifts were referenced to the solvent peak $CDCl_3$ (77.0 ppm). All photoinitiators were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis.

Synthesis of (9-ethyl-9*H*-carbazole-3,6-diyl)*bis*(phenylmethanone)



Chemical Formula: $C_{28}H_{21}NO_2$
Molecular Weight: 403.4810

$AlCl_3$ (7.20 g, 54 mmol, M = 133.34 g/mol) was added by portion to a cooled solution

of 9-ethyl-9*H*-carbazole (5.27 g, 27 mmol, M = 195.26 g/mol) and benzoyl chloride (7.6 g, 6.26 mL, 54 mmol, M = 140.57 g/mol, d = 1.211) dissolved in dry dichloromethane (DCM) (25 mL, stabilized with amylene). The solution was stirred at room temperature overnight. The solution was quenched with water. The organic phase was extracted several times with DCM. The organic phases were combined, dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was suspended in a minimum of DCM and addition of pentane precipitated a white solid that was filtered off, washed several times with pentane and dried under vacuum (8.93 g, 82% yield). ^{1}H NMR ($CDCl_3$) δ : 1.53 (t, 3H, J = 7.2 Hz), 4.48 (q, 2H, J = 7.3 Hz), 7.49-7.54 (m, 6H), 7.58-7.64 (m, 2H), 7.82-7.86 (m, 4H), 8.09 (dd, 2H, J = 8.6 Hz, J = 1.6 Hz), 8.59 (d, 2H, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ : 139, 38.2, 108.7, 122.8, 124.2, 128.3, 129.1, 129.7, 129.9, 131.9, 138.7, 143.2, 196.4; HRMS (ESI MS) m/z: theor: 403.1572 found: 403.1574 $[M+H]^+$ detected).