## **Supporting Information:**

## Design of New Type I & Type II Photoinitiators Possessing Highly Coupled Pyrene-Ketone Moieties

**Figure 1.** (A) Fluorescence quenching of <sup>1</sup>Py\_DMPA by Iod in acetonitrile/toluene (50/50); Insert: the associated Stern-Volmer treatment. (B) Cyclic voltammogram for Py\_DMPA in acetonitrile. (C) (a) absorption and (b) fluorescence spectra.



**Figure 2.** (A) Fluorescence quenching of <sup>1</sup>Py\_BP by Iod in acetonitrile/toluene (50/50). (B) Fluorescence quenching of <sup>1</sup>Py\_BP by EDB in acetonitrile/toluene (50/50).



**Figure 3.** Photolysis of a Py-BP/Iod in acetonitrile/toluene (50/50); halogen lamp exposure. UV-visible spectra recorded at different irradiation times.



**Figure 4.** (A) ESR-Spin Trapping spectra obtained after a halogen lamp irradiation of Py\_BP/Iod (in tert-butylbenzene), experimental (a) and simulated (b) spectra. (B) ESR-Spin Trapping spectra obtained after a halogen lamp irradiation of Py\_BP/EDB (in tert-butylbenzene), experimental (a) and simulated (b) spectra. Phenyl-N-*tert*-butylnitrone (PBN) is used as spin-trap.



**Figure 5.** Photopolymerization profiles of EPOX under air. Upon a halogen lamp irradiation in the presence of: (1) ITX/Iod (0.5%/2% w/w); (2) Py\_TX/Iod (0.5%/2% w/w). Sample thickness = 25 µm.



**Figure 6.** Photopolymerization profiles of TMPTA in laminate upon a halogen lamp irradiation in the presence of (1) BP/Iod (1%/2% w/w); (2) DMPA/Iod (1%/2% w/w); (3) Py\_DMPA/Iod (1%/2% w/w); (4) Py\_BP/Iod (1%/2% w/w). Sample thickness = 25  $\mu$ m.

