SUPPORTING INFORMATION:

Size exclusion chromatography experiments:

The number average molecular weights ($M_n$) and polydispersity index (PDI=$M_w/M_n$) were determined by size exclusion chromatography SEC using a Waters 515 HPLC pump equipped with 2 columns (PSS SDV LINEAR M 5 µm), and two detectors: UV/visible (Waters 486) and DRI (Waters 2414). Measurements were performed in tetrahydrofuran THF at room temperature, with a flow rate of 1 mL.min$^{-1}$. Toluene was used as a flow rate marker. Calibration was based on polystyrene standards (kit EasyCal from Polymer Laboratories $M_n$ between 580 - 377,400 g.mol$^{-1}$) and Mark-Houwink parameters (PS $K = 11.4 \times 10^{-3}$ mL.g$^{-1}$, $\alpha = 0.716$; PBA $K = 12.2 \times 10^{-3}$ mL.g$^{-1}$, $\alpha = 0.70$).[1]

For the CH$_1$/MDEA/R-Br photoinitiating system upon halogen lamp exposure in lauryl acrylate, a polymer characterized by $M_n$ of 34,000 g.mol$^{-1}$ and a PDI of 3.3 has been observed.

**Figure S1.** (A) Cyclic voltammogram of CH_1 in acetonitrile. (B) (a) Absorption and (b) fluorescence spectra of CH_2 in acetonitrile.

**Figure S2.** fluorescence spectra of CH_1 in TMPTA and EPOX.
**Figure S3.** Fluorescence spectra (normalized to 1.0 for $T^*$) in the course of the polymerization of a TMPTA/EPOX blend; initiating system CH$_1$/Iod/NVK (see text).