SUPPORTING INFORMATION FOR:

π-conjugated sulfonium-based photoacid generators: an integrated molecular approach for efficient one and two-photon polymerization

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CONTENTS

I. Some photophysical and photochemical characterization

II. Figures
I. Photophysical and photochemical characterizations

**Methods for the determination of quantum yield for acid generation.** The quantum yields for acid generation were determined upon irradiation at 405 nm using LED spotlight source (Uvata, Shanghai) equipped with a band pass filter. All irradiated PAGs dissolved in acetonitrile were previously N$_2$-degassed. The progress of the photoreaction was monitored via UV–vis absorption spectra. The absorbance at the excitation wavelength ($A_{405\text{ nm}}$) was greater than 2.5 to assume a total absorption of the incident photons. The dose rates were kept sufficiently small so that the changes of $A_{405\text{ nm}}$ were lower than 10%. The Rhodamine B (RhB) was used as a sensor of photoacid generation. The acid generation in acetonitrile was also evaluated from a calibration curve of RhB which was gradually protonated by addition of p-toluenesulfonic acid, and its molar extinction coefficient is 116000 M$^{-1}$ cm$^{-1}$ at 555 nm.

Photoacid quantum yields were calculated according the equation:

$$
\Phi_{H^+} = \frac{V_{sol} N_A}{I_{cell} S_{irr} I_0 (1 - 10^{-\Delta A_{405\text{ nm}}})} \left( \frac{\text{d}A_{555\text{ nm}}}{\text{d}t} \right)
$$

Where $V_{sol}$, $l_{cell}$ and $S_{irr}$ correspond to the volume of the irradiated solution, the optical path and the irradiated surface respectively. $N_A$ is the Avogadro number. $A_{555\text{ nm}}$ and $\varepsilon_{555\text{ nm}}$ correspond to the absorbance and the extinction coefficient of RhB. Finally, the incident light intensity at 405 nm ($I_0$) were measured by ferrioxalate actinometry.

**Methods for the determination of the maximum polymerization rates.** The polymerization rates ($R_p/[M_0]$) were determined according to the maximum value of the first derivative of the FT-RTIR curves.

Reversed-phase HPLC using a BetaBasic-18 column was analyzed by Agilent technologies 1200 series and detected at 350 nm with acetonitrile/methanol (9/1, V/V) as fluent.

**Photolysis of Para-Bz with TEA and identification of Photoproducts.** A 2 mL sample of a 0.05 M solution of Para-Bz and 10 eq. TEA in acetonitrile in a glass vessel was purged with nitrogen for 30 min, sealed, and irradiated for 1 h with a 405 nm LED lamp (1 mW/cm$^2$). The reaction mixture was poured into 5 mL of water and extracted twice with 10 mL of CH$_2$Cl$_2$. Half of the combined extract was concentrated to 10 mL under reduced pressure and analyzed by HPLC and MS. And another part was evaporated and dried in vacuum to test $^1$H NMR and compared with precursor, PrP.
II. Figures

**Figure S1.** Growth of a fluorescence band during the photolysis of Para-Bz in acetonitrile. ($\lambda_{\text{exc}}$: 405 nm).

**Figure S2.** Normalized absorption spectra of precursors in acetonitrile.
Figure S3. Evolution of $^1$H NMR spectra Para-Bz without (a) and with Et$_3$N (b) upon irradiation at 405 nm (2.0 mW cm$^{-2}$). (Solvent: CD$_3$CN).
Figure S4. $^1$HNMR spectra of photoproducts (top) and PrP (bottom) in CDCl$_3$. 
Figure S5. HPLC and MS spectra of the final photoproducts generated upon photolysis of Para-Bz in presence of TEA (10 eq.) in acetonitrile.
Figure S6. Evolution of the absorption spectra of the PAG upon irradiation at 405 nm (0.25 mW cm\(^{-2}\)). (Solvent: acetonitrile).
Figure S7. Conversion vs. time curves for cationic photopolymerization of CHO containing PAG (1 % wt). ($\lambda_{\text{exc}}$: 405 nm).
Figure S8. Two-photon polymerization voxels obtained with point-by-point exposures at various exposure powers ($\lambda_{exc}$: 800 nm, exposure duration: 10 ms. Diepoxide resin containing 0.4 wt % of PAG.). Scale bars: 5 µm.