

Supplementary information

Donor–Acceptor Complexes between Photoinitiators and Hybrid Organic–Inorganic SZ2080™ Photoresist

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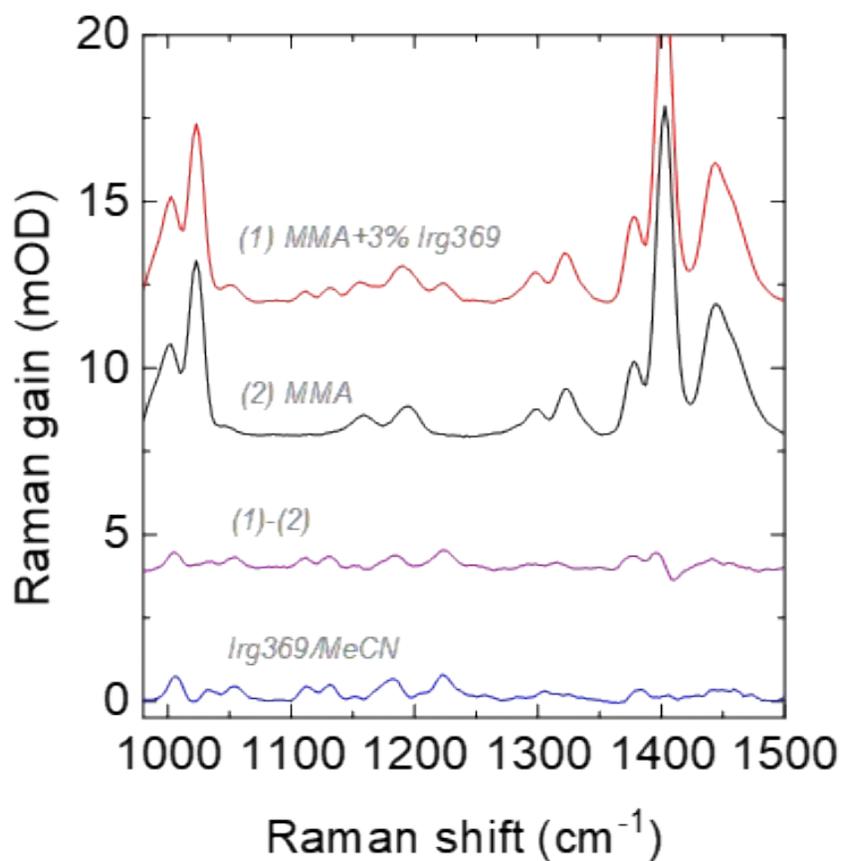


Fig. S1. SRS spectra of MMA, sensitised with IRG369. The black curve represents the SRS spectrum of the pure resin, while the red curve indicates the SRS %spectrum of the resins containing 3% photoinitiator. The violet and green curves show the difference in SRS spectra between the mixture and pure resin, as well as the SRS spectra of the pure PIs dissolved in MeCN. The Raman pump wavelength was 800 nm.

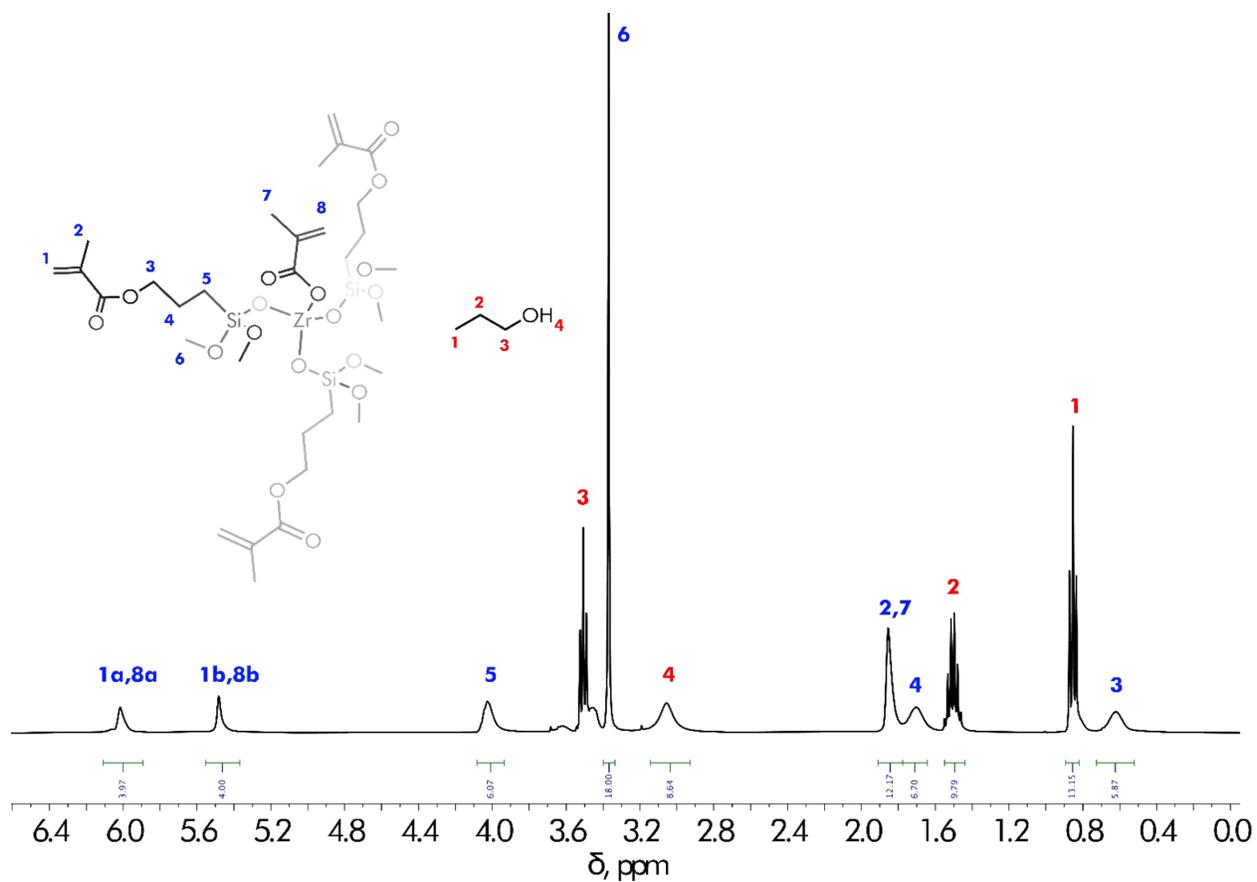


Fig. S2. ¹H NMR (CDCl₃ 400 MHz) spectrum of SZ2080™ Double bond protons 1,8 and methyl group protons 2,7 have identical chemical shifts. Sharp and well-resolved signals belong for propanol molecules.

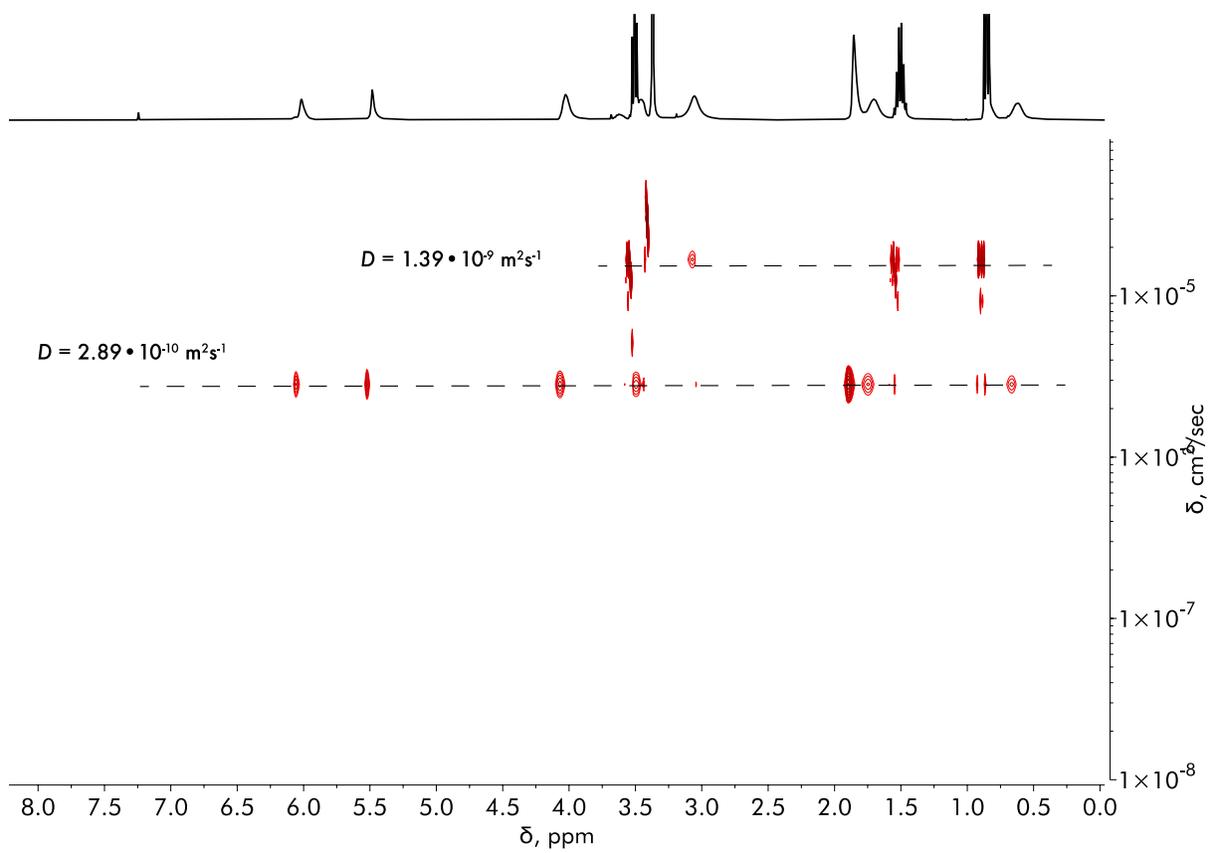


Fig. S3. DOSY (CDCl_3 , 400 MHz) spectrum of SZ2080TM. A higher value of the diffusion coefficient for the propanol signals confirms that it is not bound to zirconium metal.

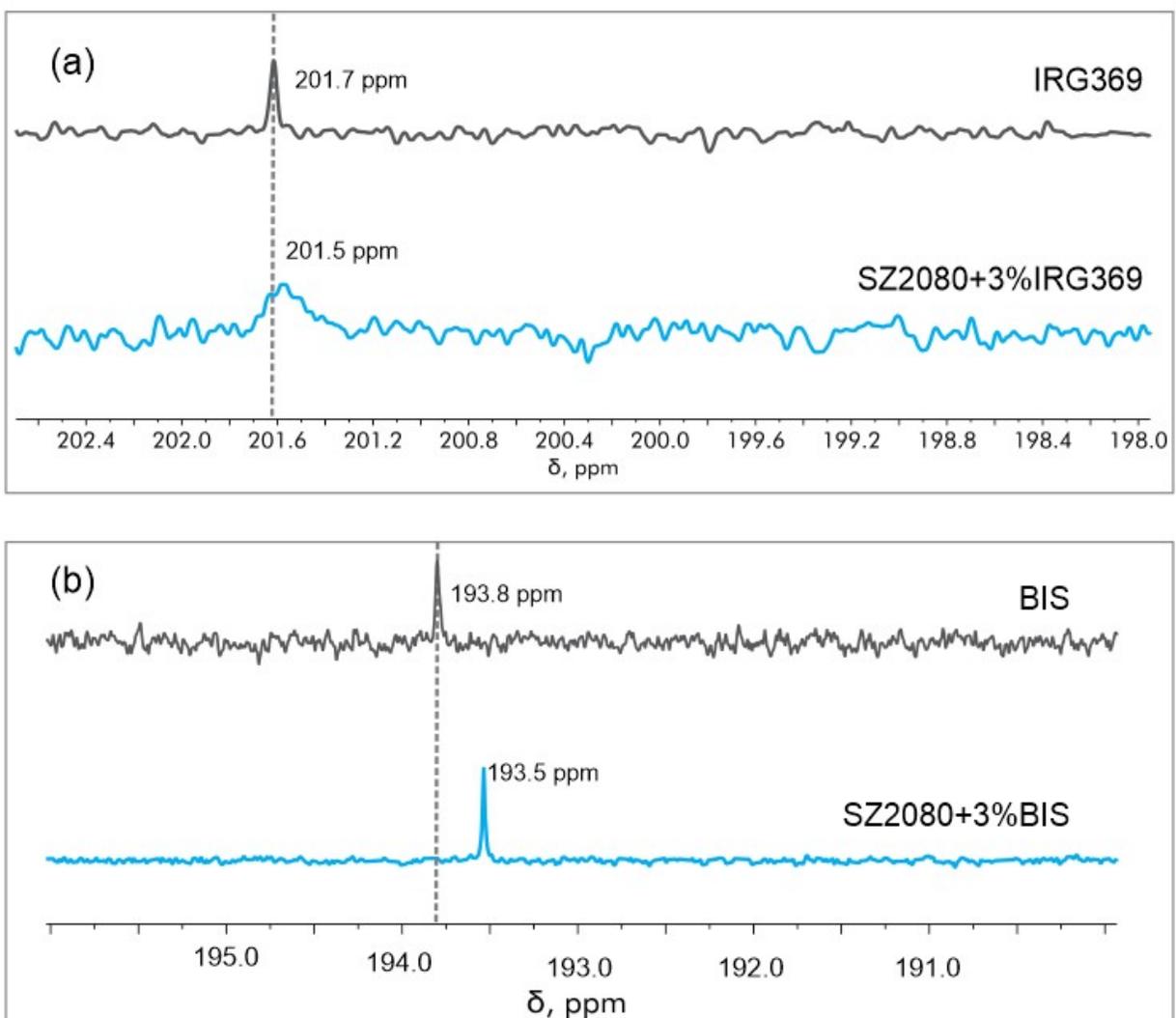


Fig. S4. $^{13}\text{C}(\text{C}=\text{O})$ NMR spectra (CD_3CN , 101 MHz) of (a) IRG369 and SZ2080TM + 3 wt% Irg369 and (b) Irg369 and SZ2080TM + 3 wt% BIS.

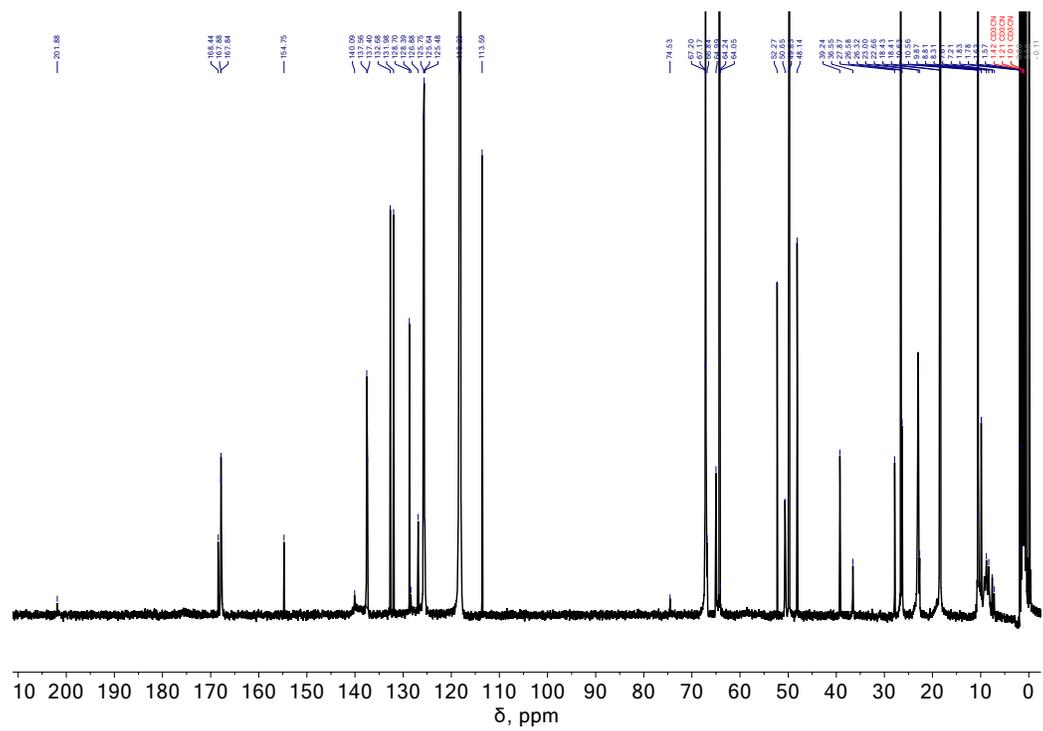
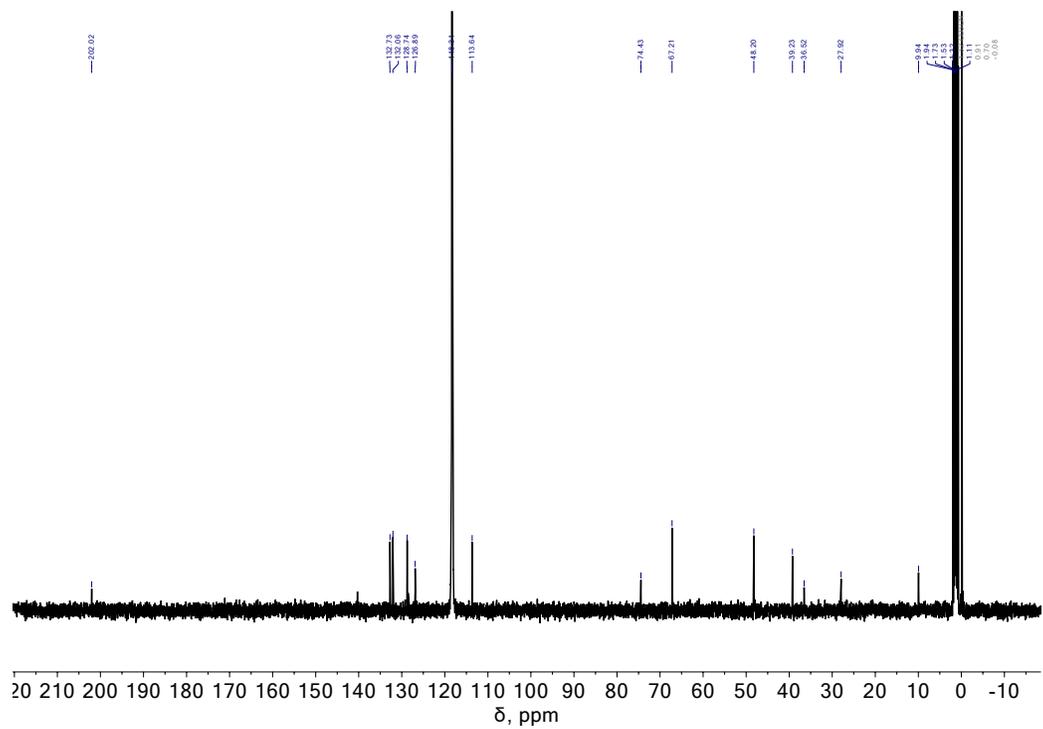


Fig. S5. ^{13}C NMR (CD_3CN , 101 MHz) of Irg369 (top) and SZ2080TM + 3 wt% IRG369 (bottom).

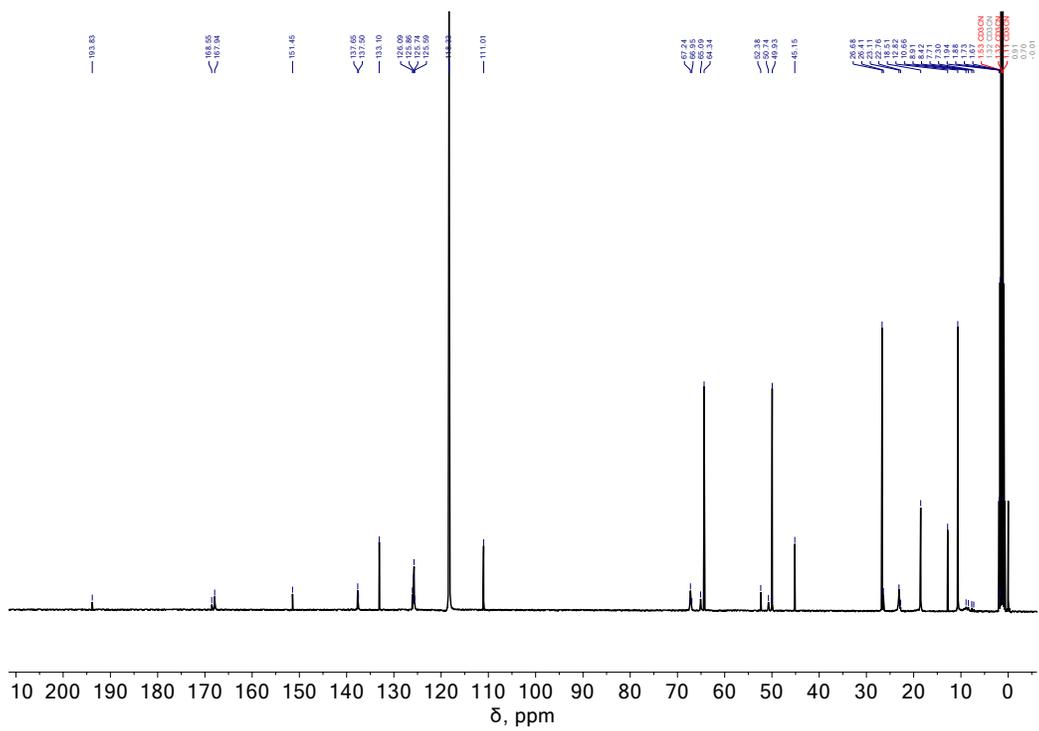
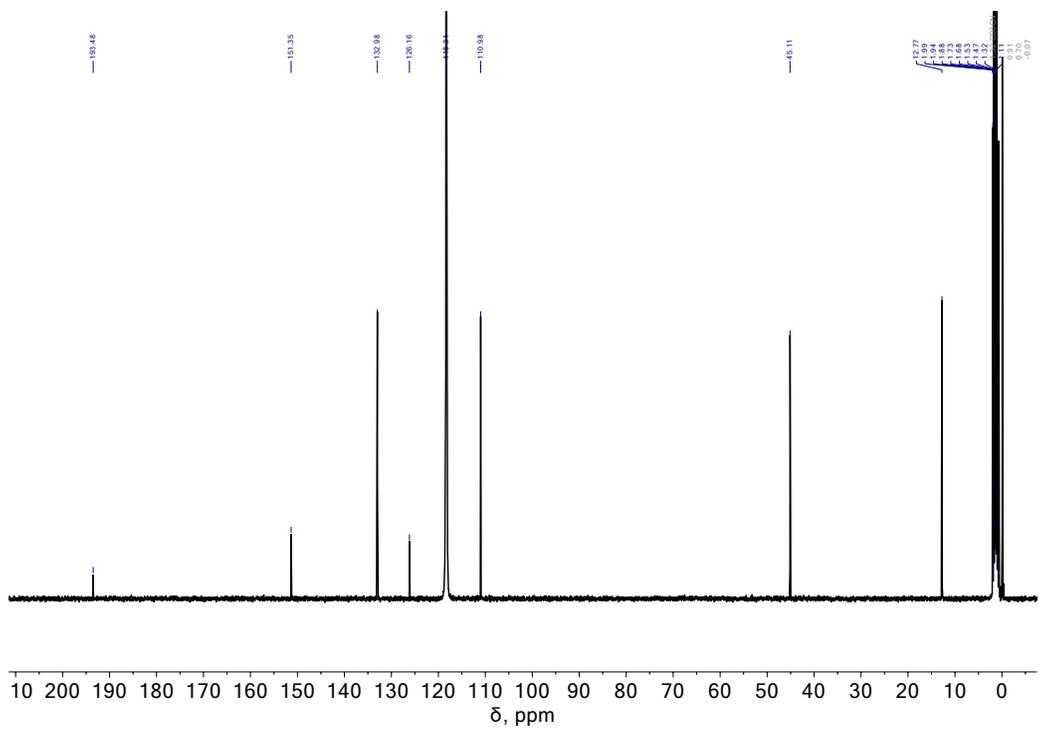


Fig. S6. ¹³C NMR (CD₃CN, 101 MHz) of BIS (top) and SZ2080™ + 3 wt% BIS (bottom).

Table S1. Assignment of the Raman frequencies by DFT calculations of SZ2080TM.

Raman (cm ⁻¹)	DFT (cm ⁻¹)	Assignment
380	345	$\delta(\text{CCC})$, $\delta(\text{COO})$, $\nu(\text{Zr-O})$
605	605	$\delta(\text{COO})$, $\nu(\text{Zr-O})$
860	865, 881	$\delta(\text{COO})$, $\delta(\text{CCC})$, $\nu(\text{Zr-O})$
1035	1023	$r(\text{CH}_3)$, $\nu(\text{C-C})$
1298	1306	$\nu(\text{C-C})$, $\nu(\text{C-O})$
1406	1406	$\delta_s(\text{CH}_3)$, $\nu(\text{C-CH}_3)$
1454	1442	$\delta(\text{CH}_2)$, $\delta(\text{CH}_3)$
1650	1656, 1674	$\nu(\text{C=C})$
1736	1794	$\nu(\text{C=O})$

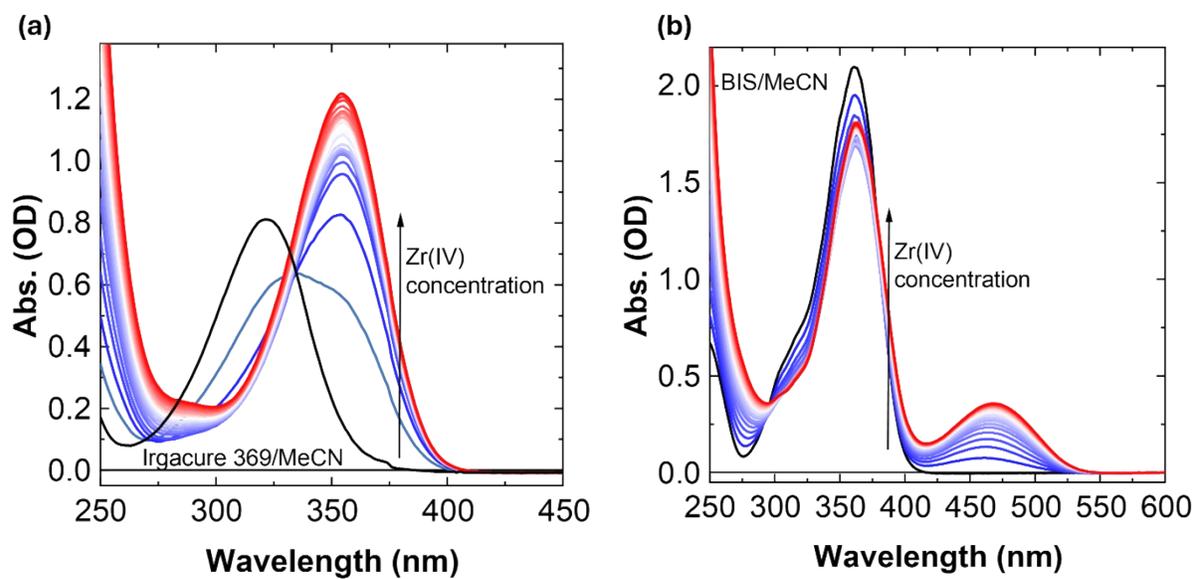


Fig. S7 Absorption changes of (a) IRG369 and (b) BIS photoinitiators upon titration with SZ2080TM.

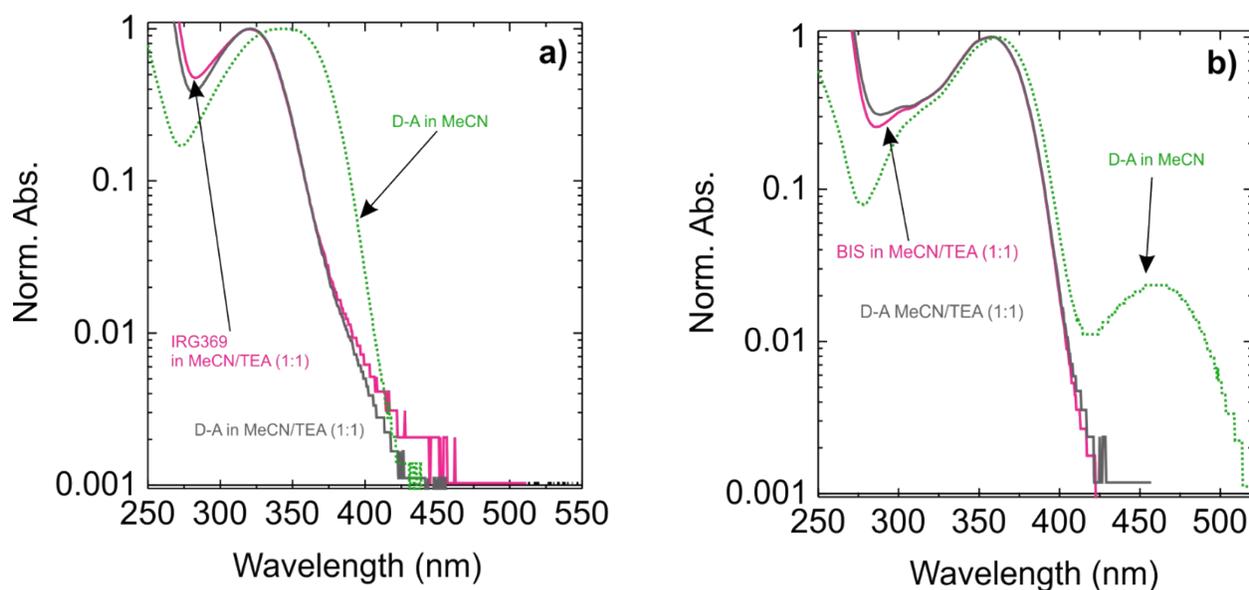


Fig. S8 Ground-state absorption spectra of (a) IRG369-SZ2080™ and (b) BIS-SZ2080™ complexes (D-A), along with the absorption spectra of the corresponding pure PIs in MeCN and MeCN/TEA solutions. All TEA mixtures were prepared with a 1:1 ratio of MeCN to TEA. TEA denotes triethylamine.

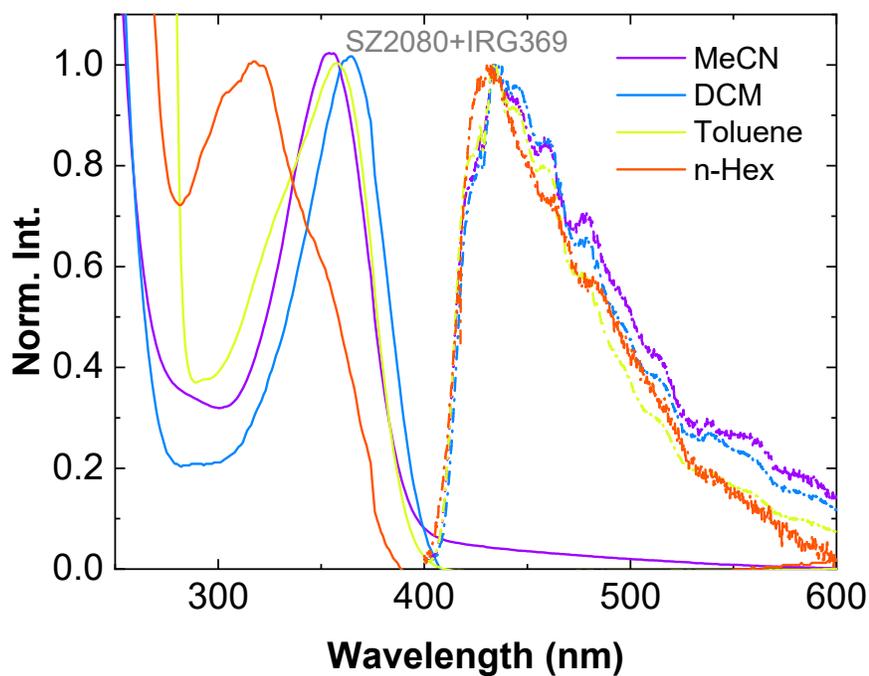


Fig. S9. Ground-state absorption and fluorescence spectra of IRG369-SZ2080™ complexes obtained in different solvents.

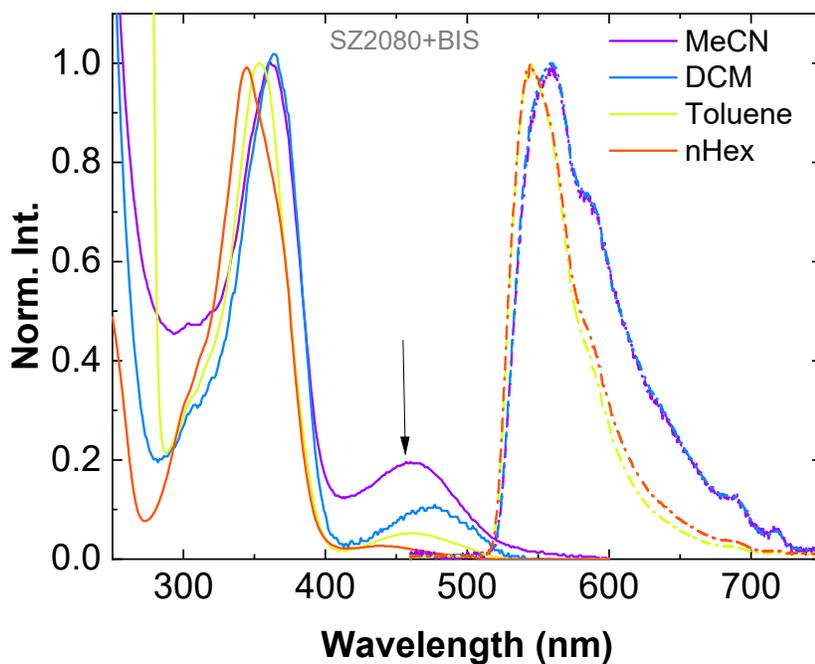


Fig. S10. Ground-state absorption and emission spectra of BIS-SZ2080TM complexes obtained in different solvents.

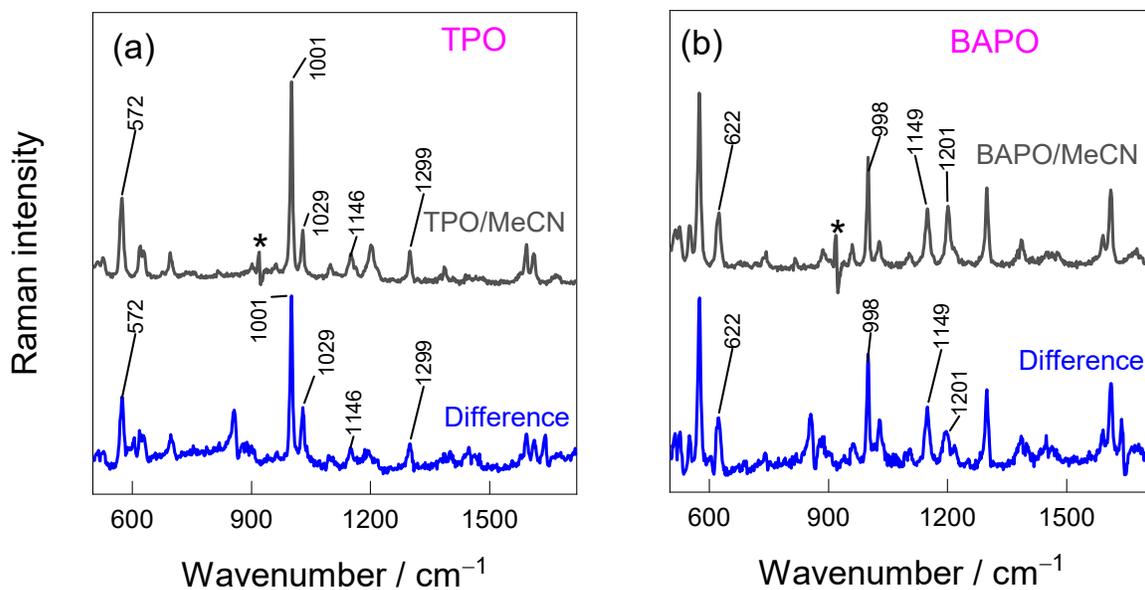


Fig. S11 Comparison of Raman spectra ($\lambda_{\text{ex}} = 830 \text{ nm}$) of SZ2080TM sensitised with 3% of (a) TPO and (b) BAPO photoinitiators. The blue curve shows the difference spectrum between sensitised and unsensitised SZ2080TM, while the grey curve represents the Raman spectrum of the photoinitiator in MeCN. The asterisks indicate the artefacts due to the subtraction of the solvent.