Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Imidazole based dual photo/thermal initiators for highly efficient radical polymerization under air with metal-free approach

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Experimental Section

All the four imidazoles (***1****: 2-hydroxyethyl 3-(20ethyl-4-methyl-1H-imidazol-1-yl)propanoate;* ***2****: 2-Methylimidazole;* ***3****: 2-Ethyl-4-Methylimidazle;* ***4****: 1-Methylimidazole*) were purchased from sigma-Aldrich or TCI Chemicals. Di-tert-butyl-diphenyl iodonium hexafluorophosphate (Iod) was obtained from Lambson Ltd (UK). Trimethylolpropane triacrylate (TMPTA) and TA were purchased from Allnex (France). All the reactants were selected with high purity and used as received

UV-visible absorption spectra were measured by JASCO V730 spectrophotometer.

The photopolymerization was evaluated by Real-Time Fourier Transformed Infrared Spectroscopy JASCO FTIR-4100. Specific procedure: the sample was injected into a circular mold (10 mm inner diameter) that was pasted onto polypropylene film. Then it was placed on a sample holder in a horizontal accessory (transmission mode). Real-Time Fourier Transformed Infrared Spectrometer (RT-FTIR) was used to follow the C=C double bond conversion (for both acrylate functionalities) versus time for polymerizations of 3.5 mm thick samples in laminate. The decrease of the C=C double bond at 6130–6200 cm^{-1} was followed. A LED@405 nm having an intensity of 0.11 W/cm^2 at the sample position was used for the photo-polymerization experiments.

Different monomer formulations (≈10 mg) in the presence of CTCs were inserted in an aluminum 100 μL crucible. Thermal polymerization (Mettler-Toledo DSC) was carried out from 0 to 250 °C at a heating rate of 10 °C /min under nitrogen flow (100 mL/min).

DLW experiment: The letter patterns were produced through the computer-controlled movement of laser diode (CNI laser diode, wavelength**:** 405 nm and light intensity: 0.11 W) (spot size ~50 μm, The x-y resolution can be 50 μm (size of the laser beam)) under air, the printing time is about 3 min and the pattern was characterized by numerical optical microscope (OLYMPUS DSX-HRSU).

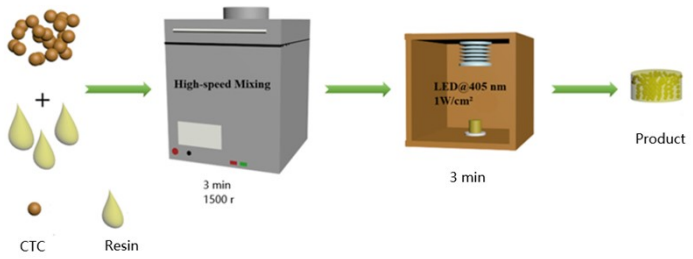
3D printing experiment: The object was obtained by 3D printer PHOTON S purchased from Anycubic (China). The wavelength of light source is 405 nm, $I < 5$ mW/cm^2 (low optical density), detailed parameter is as follows (Figure S8): the thickness of each layer is 20 um, exposure time is 120 s and 100 layers, the whole printing time is

approximately 3.5 h.

Frontier molecular orbital calculations were performed by the Gaussian 03 suite of programs.[1,2] Simulation of the UV absorption spectra and the triplet state energy levels for the compounds were calculated with the time-dependent density functional theory at the MPW1PW91/6-31G* level of theory on the relaxed geometries calculated at the UB3LYP/6-31G* level of theory.

The preparation of composites:
Glass and carbon fiber composites were produced successfully using imidazole based CTC/TMPTA system (CTC **3**, 3 wt%). The glass fibers are characterized by 1177 g/m² from Sicomin. The prepregs were composed of resin/glass fiber or resin/carbon fiber (50/50, wt%/wt% for both) as usual. To be specific, weighing 3 g glass fiber (carbon fiber), then cut into 3.5 cm x 4 cm pieces and stack several layers, add 3 g of resin formulation to moisten, then place between two clear films and flatten with a press (well impregnated). After preparation of prepregs, they were irradiated using LED@395 nm（395 nm LED-surface (area) light source was purchased from TaoYuan, China, the distance from the samples of composite materials (laminates) into a LED@395 nm is about 5 cm, and the light intensity of LED@395 nm is 4 W/cm^2）to initiate the photopolymerization of TMPTA in surface. Then, the prepregs were heated at 85 °C in oven for 10 min to induce the polymerization of TMPTA in depth. Fully cured glass and carbon fiber composites were obtained (see Figure 4B). The surface and inside of the composites are hard and nonsticky.

The procedure of photo curing experiment:
First of all, we prepared the resin formulation of TMPTA within 3% CTC 3 (based on 4 g monomer). Then it is mixed well by high speed stirring or stirrer. After that, in a LED-curing box, a mold filled with the investigated resin was placed vertically under the light (LED@405 nm for 3 min; 1 W/cm²) (Scheme below). The polymerized products were used to measure the Depth of Cure (DOC) with an Absolute LCD Digimatic Indicator (Mitutoyo).



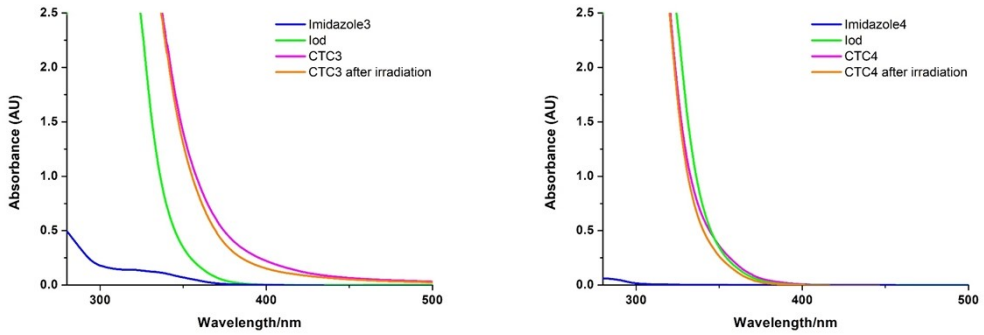
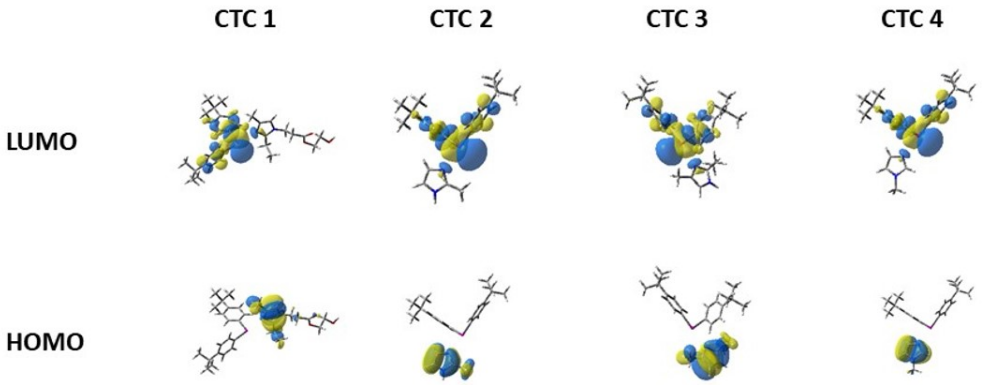


Figure S1. UV–visible absorption spectra of imidazole 3&4, Iod salt and CTC 3&4 in dichloromethane (40 mM imidazole and 20 mM Iod).



	Lowest energy transition			
Iodonium salt	4.58 ev	4.58 ev	4.58 ev	4.58 ev
Imidazole	5.03 ev	6.66 ev	6.53 ev	6.69 ev
CTC	3.92 ev	4.32 ev	4.03 ev	4.57 ev

Figure S2. LUMO and HOMO of CTCs based on TD-DFT calculations.

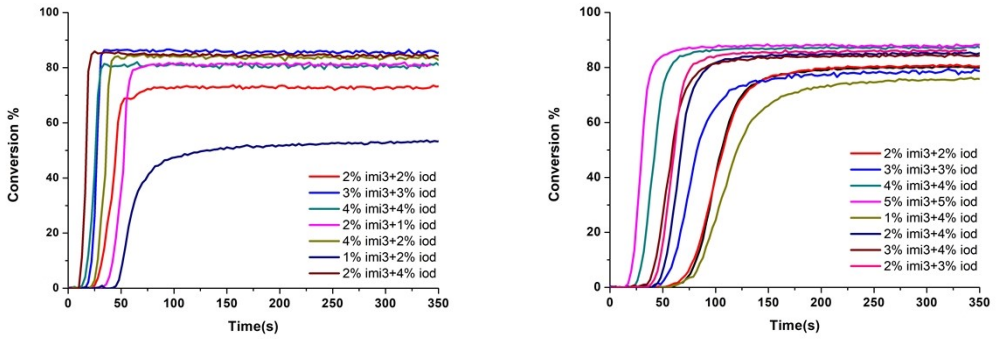


Figure S3. The optimization of photoinitiating performance by CTC **3** for TMPTA (left) and TA (right) respectively. (various amounts imidazole 3/Iod salt)

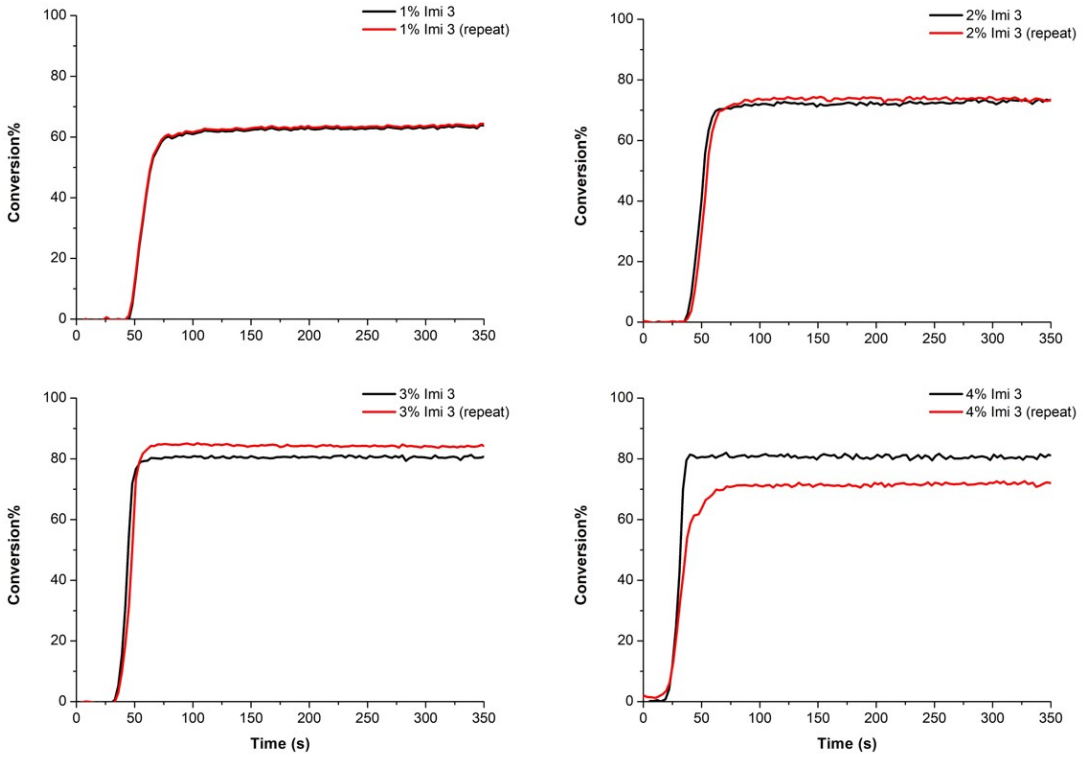


Figure S4. The photoinitiating performance by CTC **3** for TMPTA. (a fixed 2% Iod, error point in Figure 2B, dotted box)

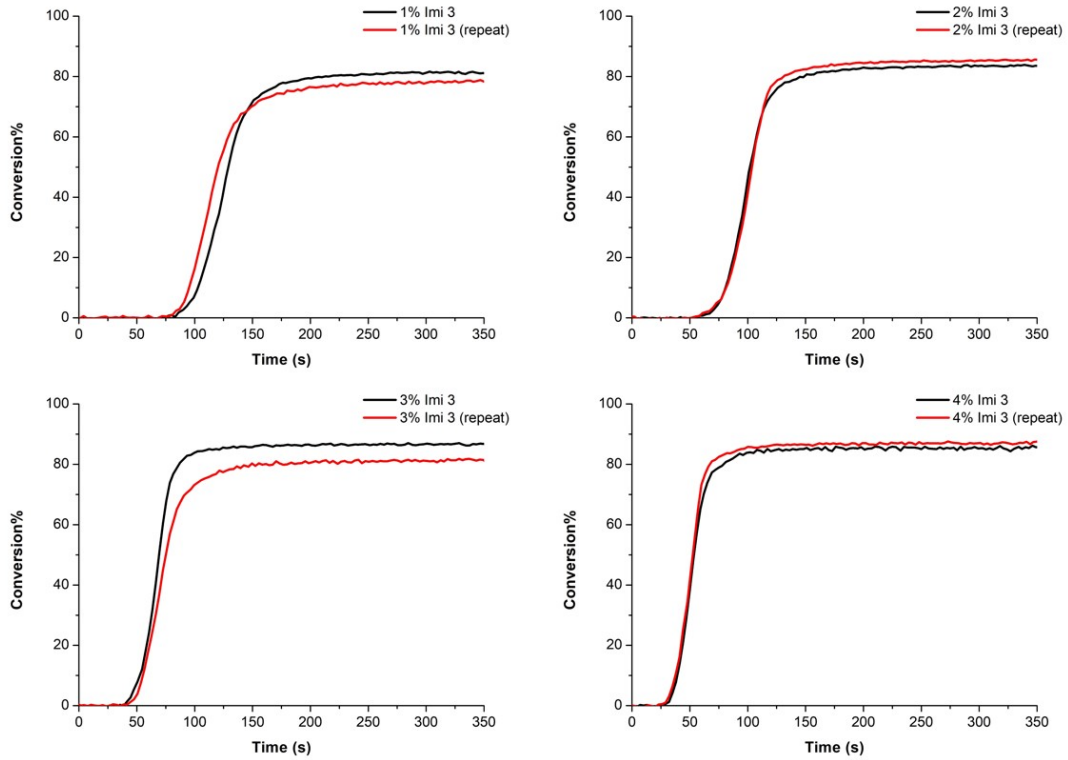
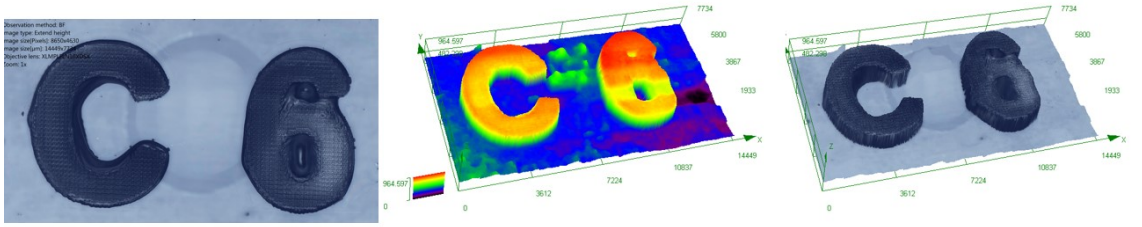
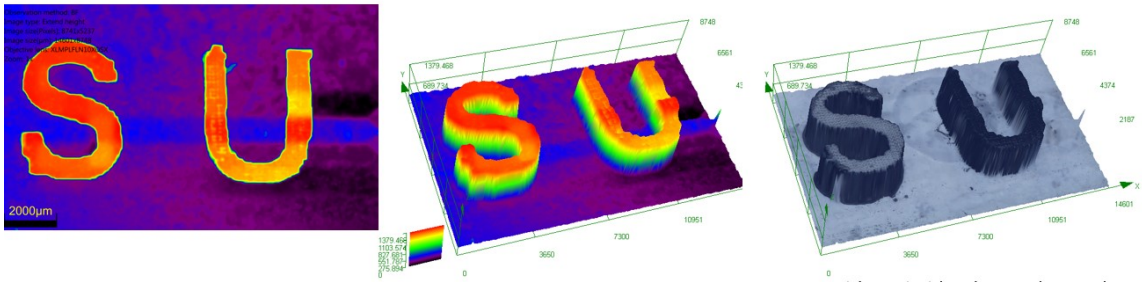


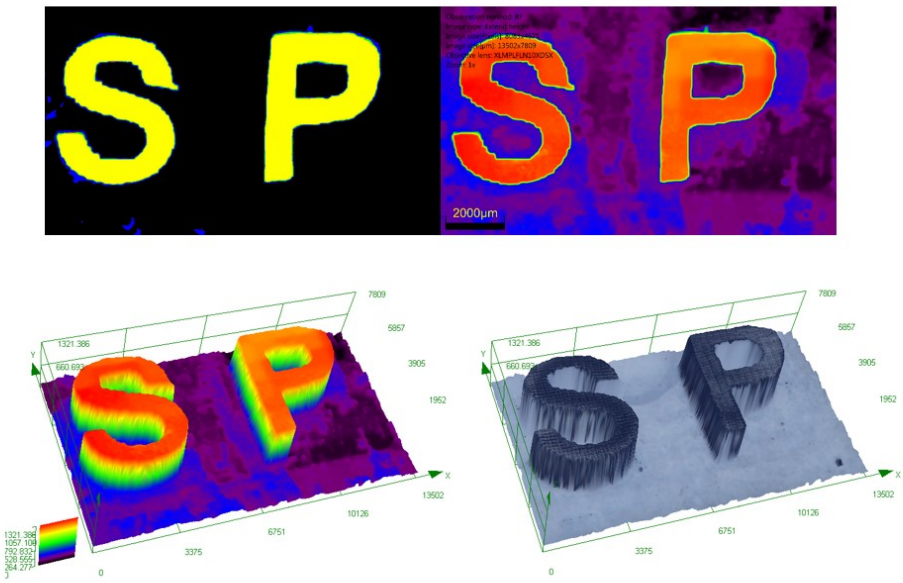
Figure S5. The photoinitiating performance by CTC **3** for TA. (a fixed 4% Iod, error point in Figure 2E, dotted box)



For TMPTA with 1% imidazole 3 and 1% Iod



For TMPTA with 2% imidazole 3 and 2% Iod



For TMPTA with 3% imidazole 3 and 3% Iod

Figure S6. Optical microscopy of the 3D patterns printed from TMPTA with 1-3% CTC **3**. Top surface morphology and 3D overall appearance in color and black-and-white patterns. The scale bar is 2000 μm. The thickness of the z-direction can be ~ 1.4 mm and the unit in plane has been added.

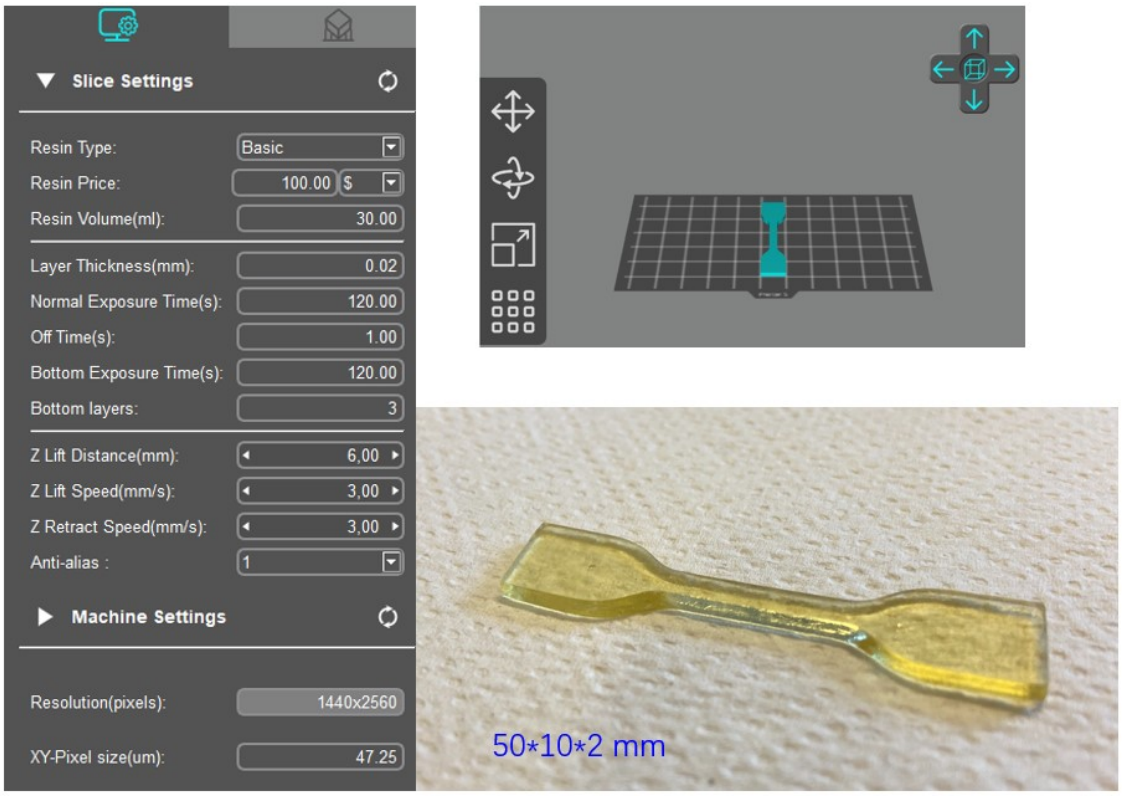


Figure S7. Detailed parameters and 3D object obtained by printing with our formulation (TMPTA with 2% wt% CTC **3**, Object: 50 mm × 10 mm × 2 mm).

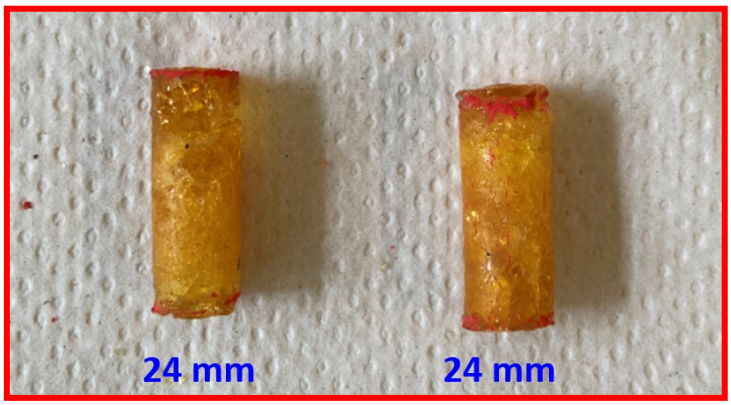


Figure S8. DoC of poly(TMPTA) with CTC **3** (2% wt) can reach 24 mm for 1.5 min (left) and 3 min (right) under 405 nm @LED irradiation.

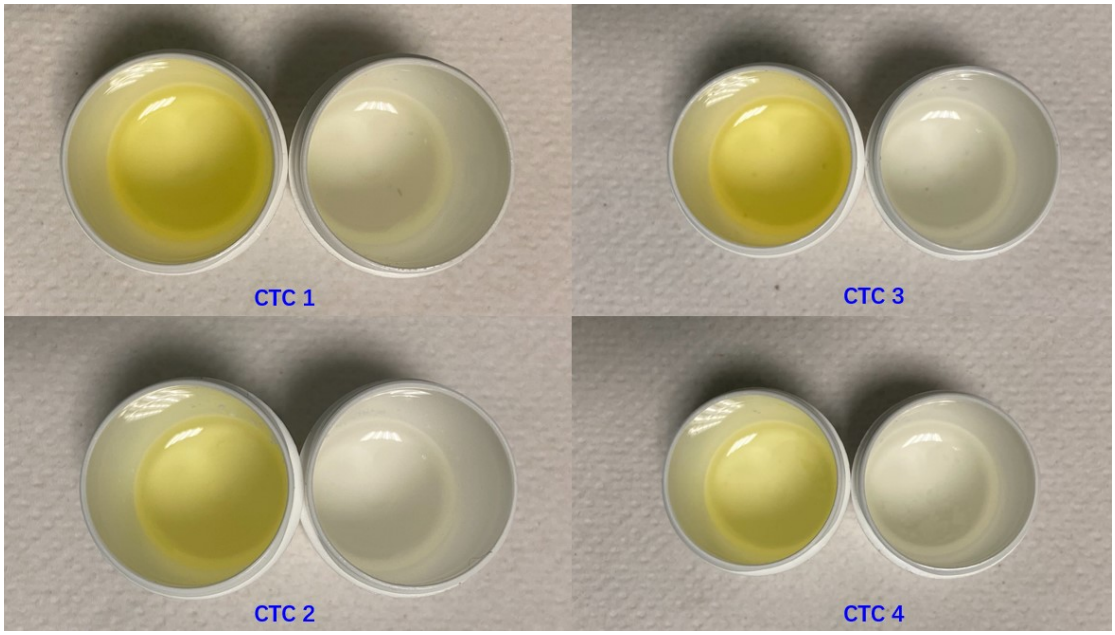


Figure S9. The color pictures of different formulations with CTC **1-4** in TMPTA (Left) or TA (Right).

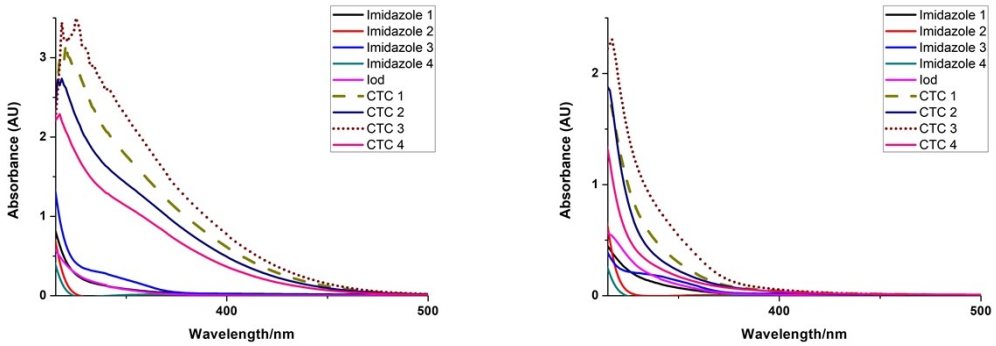


Figure S10. UV–visible absorption spectra of CTC **1-4** (2% wt%) in TMPTA (Left) and TA (Right).

Reference

1. B. James and A. Frisch, Gaussian, Incorporated, 1996.
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. W. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen,M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian 03, Revision B-2, Gaussian Inc., Pittsburgh, PA, 2003.