

## Supporting Information

### **Novel ketone derivatives based photoinitiating systems for free radical polymerization under mild conditions and 3D printing**

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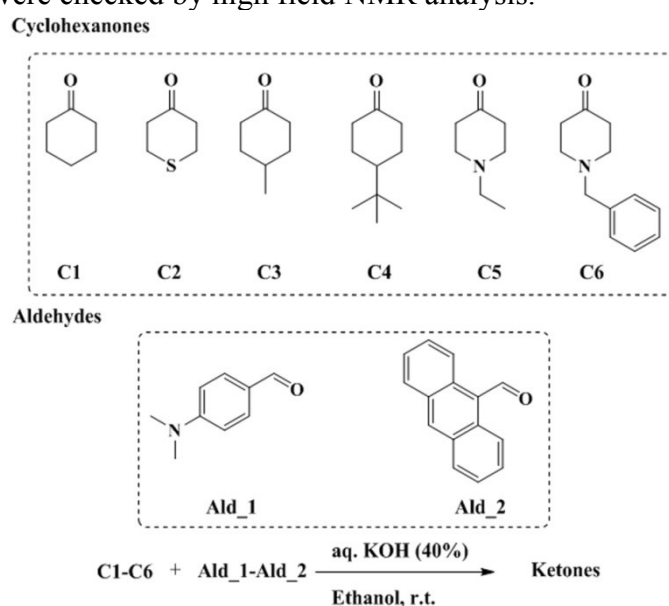
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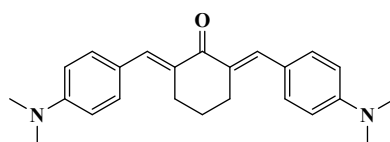
1. Chemical synthesis.
2. Formulation preparation.
3. UV-vis absorption property.
4. Theoretical computation.
5. Photopolymerization.
6. Steady state photolysis.

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole:  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  (100 MHz). The  $^1\text{H}$  chemical shifts were referenced to the solvent peaks: DMSO (2.49 ppm),  $\text{CDCl}_3$  (7.26 ppm) and the  $^{13}\text{C}$  chemical shifts were referenced to the solvent peaks: DMSO (49.5 ppm),  $\text{CDCl}_3$  (77.0 ppm), respectively. All photoinitiators were prepared with analytical purity up to accepted standards for new organic compounds (>98%), which were checked by high field NMR analysis.



**Scheme S1** Chemical synthesis for the twelve ketones.

Synthesis of 2,6-*bis*((*E*)-4-(dimethylamino)benzylidene)cyclohexan-1-one (Ami-1)

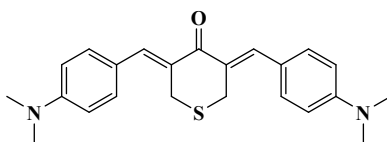


Chemical Formula:  $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}$   
Molecular Weight: 360.5010

Cyclohexanone (0.98 g, 10 mmol,  $M = 98.14$  g/mol) and 4-dimethylaminobenzaldehyde (2.98 g, 20 mmol,  $M = 149.19$  g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of  $\text{SiO}_2$  using dichloromethane as the eluent. The solvent was removed under reduced pressure.

Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (3.12 g, 87% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.77-1.85 (m, 2H), 2.91-2.96 (m, 4H), 3.02 (s, 12H), 6.72 (d, 4H, J = 8.7 Hz), 7.44 (d, 4H, J = 8.7 Hz), 7.76 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 23.2, 28.7, 40.2, 111.7, 124.4, 132.4, 132.5, 137.0, 150.3, 190.1; HRMS (ESI MS) m/z: theor: 360.2202 found: 360.2203 (M<sup>+</sup> detected).

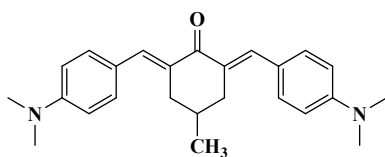
Synthesis of 3,5-bis((Z)-4-(dimethylamino)benzylidene)tetrahydro-4H-thiopyran-4-one (Ami-2)



Chemical Formula: C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>OS  
Molecular Weight: 378.5340

Tetrahydro-4H-thiopyran-4-one (1.17 g, 10 mmol, M = 116.18 g/mol) and 4-dimethylaminobenzaldehyde (2.98 g, 20 mmol, M = 149.19 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO<sub>2</sub> using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (3.44 g, 91% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.03 (s, 12H), 3.97 (s, 4H), 6.72 (d, 4H, J = 8.8 Hz), 7.37 (d, 4H, J = 8.8 Hz), 7.75 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 30.4, 40.2, 111.9, 130.1, 132.3, 137.2, 150.5, 188.6; HRMS (ESI MS) m/z: theor: 378.1766 found: 378.1764 (M<sup>+</sup> detected).

Synthesis of 2,6-bis((E)-4-(dimethylamino)benzylidene)-4-methylcyclohexan-1-one (Ami-3)

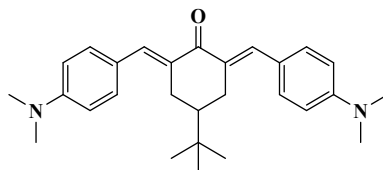


Chemical Formula: C<sub>25</sub>H<sub>30</sub>N<sub>2</sub>O  
Molecular Weight: 374.5280

4-Methylcyclohexan-1-one (1.12 g, 10 mmol, M = 112.17 g/mol) and 4-dimethylaminobenzaldehyde (2.98 g, 20 mmol, M = 149.19 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO<sub>2</sub> using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane

precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (3.07 g, 82% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.10 (d, 3H, J = 6.5 Hz), 1.85-1.93 (m, 1H), 2.46-2.54 (m, 2H), 3.02 (s, 12H), 3.07-3.19 (m, 2H), 6.73 (d, 4H, J = 8.6 Hz), 7.45 (d, 4H, J = 8.6 Hz), 7.76 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 21.9, 29.5, 36.9, 40.2, 111.7, 124.3, 131.7, 132.4, 137.2, 150.4, 189.8; HRMS (ESI MS) m/z: theor: 374.2358 found: 374.2354 (M<sup>+</sup> detected).

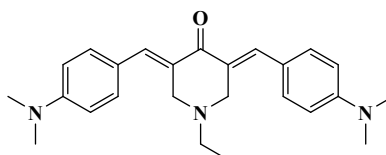
Synthesis of 4-(*tert*-butyl)-2,6-bis((*E*)-4-(dimethylamino)benzylidene)cyclohexan-1-one (Ami-4)



Chemical Formula: C<sub>28</sub>H<sub>36</sub>N<sub>2</sub>O  
Molecular Weight: 416.6090

4-(*Tert*-butyl)cyclohexan-1-one (1.54 g, 10 mmol, M = 154.25 g/mol) and 4-dimethylaminobenzaldehyde (2.98 g, 20 mmol, M = 149.19 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO<sub>2</sub> using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (3.46 g, 83% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.00 (s, 9H), 1.47-1.56 (m, 1H), 2.42-2.48 (m, 2H), 3.03 (s, 12H), 3.16-3.20 (m, 2H), 6.75 (d, 4H, J = 8.3 Hz), 7.45 (d, 4H, J = 8.3 Hz), 7.73 (d, 2H, J = 2.2 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 27.5, 29.7, 32.5, 40.2, 44.4, 111.8, 132.4, 136.9, 150.3, 190.2; HRMS (ESI MS) m/z: theor: 416.2828 found: 416.2828 (M<sup>+</sup> detected).

Synthesis of 3,5-bis((*E*)-4-(dimethylamino)benzylidene)-1-ethylpiperidin-4-one (Ami-5)

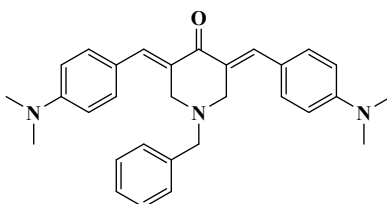


Chemical Formula: C<sub>25</sub>H<sub>31</sub>N<sub>3</sub>O  
Molecular Weight: 389.5430

1-Ethylpiperidin-4-one (1.27 g, 10 mmol, M = 127.19 g/mol) and 4-dimethylaminobenzaldehyde (2.98 g, 20 mmol, M = 149.19 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was

dissolved in dichloromethane and the solution was filtered on a plug of SiO<sub>2</sub> using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (3.70 g, 95% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.03 (t, 3H, J = 7.1 Hz), 2.59 (q, 2H, J = 7.1 Hz), 2.95 (s, 12H), 3.81 (s, 4H), 6.64 (d, 4H, J = 8.9 Hz), 7.28 (d, 4H, J = 8.9 Hz), 7.71 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 12.5, 40.1, 54.5, 111.7, 123.5, 132.5, 136.9, 150.6, 186.8; HRMS (ESI MS) m/z: theor: 389.2467 found: 389.2470 (M<sup>+</sup> detected).

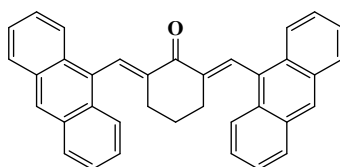
Synthesis of 1-benzyl-3,5-bis((E)-4-(dimethylamino)benzylidene)piperidin-4-one (Ami-6)



Chemical Formula: C<sub>30</sub>H<sub>33</sub>N<sub>3</sub>O  
Molecular Weight: 451.6140

1-Benzylpiperidin-4-one (1.90 g, 10 mmol, M = 189.26 g/mol) was dissolved in a mixture of ethanol (20 mL) and water (10 mL). 4-Dimethylaminobenzaldehyde (2.98 g, 20 mmol, M = 149.19 g/mol) and NaOH 1M (10 mL) were then added at 0 °C. During stirring, a sticky solid formed so that THF (20-30 mL) was added to maintain the stirring of the solution. The solution was stirred at room temperature overnight. The yellow precipitate was filtrated off, washed with ethanol and dried under vacuum (3.83 g, 85% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.01 (s, 12H), 3.72-3.77 (m, 2H), 3.91 (brs, 4H), 6.68 (d, 4H, J = 8.9 Hz), 7.19-7.32 (m, 9H), 7.77 (brs, 2H); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ: 2.98 (s, 12H), 3.75 (s, 2H), 3.79 (s, 4H), 6.74 (d, 4H, J = 8.9 Hz), 7.19-7.23 (m, 1H), 7.27-7.33 (m, 8H), 7.50 (s, 2H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>) δ: 25.1, 54.6, 67.0, 111.8, 122.2, 127.1, 128.2, 128.8, 129.1, 132.3, 134.9, 138.0, 150.6, 185.7; HRMS (ESI MS) m/z: theor: 451.2624 found: 451.2626 (M<sup>+</sup> detected).

Synthesis of 2,6-bis(anthracen-9-ylmethylene)cyclohexan-1-one (Anth-1)

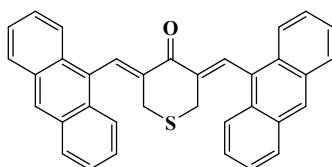


Chemical Formula: C<sub>36</sub>H<sub>26</sub>O  
Molecular Weight: 474.6030

Cyclohexanone (0.98 g, 10 mmol, M = 98.14 g/mol) and anthracene-9-carbaldehyde (4.12 g, 20 mmol, M = 206.24 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in

dichloromethane and the solution was filtered on a plug of SiO<sub>2</sub> using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (3.74 g, 79% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.46-1.55 (m, 2H), 2.27-2.31 (m, 4H), 7.49-7.57 (m, 8H), 8.04-8.11 (m, 8H), 8.48 (s, 2H), 8.68 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 22.5, 25.6, 28.6, 125.4, 125.9, 126.0, 127.4, 128.9, 129.1, 130.5, 131.3, 135.8, 140.9, 188.6; HRMS (ESI MS) m/z: theor: 474.1984 found: 474.1982 (M<sup>+</sup> detected).

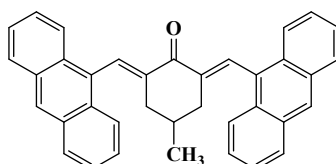
Synthesis of 3,5-bis(anthracen-9-ylmethylene)tetrahydro-4H-thiopyran-4-one (Anth-2)



Chemical Formula: C<sub>35</sub>H<sub>24</sub>OS  
Molecular Weight: 492.6360

Tetrahydro-4H-thiopyran-4-one (1.17 g, 10 mmol, M = 116.18 g/mol) and anthracene-9-carbaldehyde (4.12 g, 20 mmol, M = 206.24 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO<sub>2</sub> using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (4.04 g, 82% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.32 (s, 4H), 7.50-7.60 (m, 8H), 8.05-8.12 (m, 8H), 8.49 (s, 2H), 8.68 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 30.7, 125.5, 125.6, 126.4, 127.9, 129.0, 129.16, 129.18, 131.3, 135.4, 138.2, 187.2; HRMS (ESI MS) m/z: theor: 492.1548 found: 492.1544 (M<sup>+</sup> detected).

Synthesis of 2,6-bis(anthracen-9-ylmethylene)-4-methylcyclohexan-1-one (Anth-3)

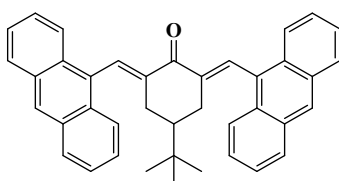


Chemical Formula: C<sub>37</sub>H<sub>28</sub>O  
Molecular Weight: 488.6300

4-Methylcyclohexan-1-one (1.12 g, 10 mmol, M = 112.17 g/mol) and anthracene-9-carbaldehyde (4.12 g, 20 mmol, M = 206.24 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was

dissolved in dichloromethane and the solution was filtered on a plug of SiO<sub>2</sub> using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (4.15 g, 85% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.58 (d, 3H, J = 6.6 Hz), 1.74-1.81 (m, 1H), 2.01-2.08 (m, 2H), 2.28-2.32 (m, 2H), 7.50-7.56 (m, 8H), 8.04-8.13 (m, 8H), 8.48 (s, 2H), 8.68 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 20.8, 28.8, 36.4, 125.39, 125.43, 125.7, 126.0, 127.3, 128.88, 128.92, 129.1, 129.2, 130.6, 131.2, 131.3, 136.2, 140.1, 188.3; HRMS (ESI MS) m/z: theor: 488.2140 found: 488.2142 (M<sup>+</sup> detected).

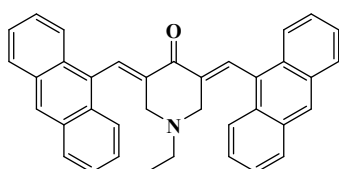
Synthesis of 2,6-bis(anthracen-9-ylmethylene)-4-(*tert*-butyl)cyclohexan-1-one (Anth-4)



Chemical Formula: C<sub>40</sub>H<sub>34</sub>O  
Molecular Weight: 530.7110

4-(*Tert*-butyl)cyclohexan-1-one (1.54 g, 10 mmol, M = 154.25 g/mol) and anthracene-9-carbaldehyde (4.12 g, 20 mmol, M = 206.24 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO<sub>2</sub> using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (4.72 g, 89% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.33 (s, 9H), 1.49-1.56 (m, 1H), 1.98-2.04 (m, 2H), 2.39-2.43 (m, 2H), 7.49-7.55 (m, 8H), 8.05-8.12 (m, 8H), 8.48 (s, 2H), 8.64 (d, 2H, J = 2.4 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 26.7, 29.6, 32.1, 44.0, 125.40, 125.41, 125.7, 125.9, 125.95, 126.01, 127.2, 130.5, 131.3, 135.8, 140.9, 188.8; HRMS (ESI MS) m/z: theor: 530.2610 found: 530.2611 (M<sup>+</sup> detected).

Synthesis of 3,5-bis(anthracen-9-ylmethylene)-1-ethylpiperidin-4-one (Anth-5)

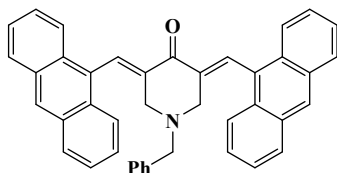


Chemical Formula: C<sub>37</sub>H<sub>29</sub>NO  
Molecular Weight: 503.6450

1-Ethylpiperidin-4-one (1.27 g, 10 mmol, M = 127.19 g/mol) and anthracene-9-carbaldehyde (4.12 g, 20 mmol, M = 206.24 g/mol) and NaOH 1 M (10 mL) were

dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO<sub>2</sub> using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (4.17 g, 83% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.49 (t, 3H, J = Hz), 2.17 (brs, 2H), 3.20 (brs, 4H), 7.50-7.57 (m, 8H), 8.04-8.11 (m, 8H), 8.49 (s, 2H), 8.74 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 11.8, 50.5, 54.1, 68.0, 125.5, 125.7, 126.2, 127.7, 128.9, 129.0, 129.5, 135.5, 137.6, 185.9; HRMS (ESI MS) m/z: theor: 502.2297 found: 502.2298 (M<sup>+</sup> detected).

#### Synthesis of 3,5-bis(anthracen-9-ylmethylene)-1-benzylpiperidin-4-one (Anth-6)



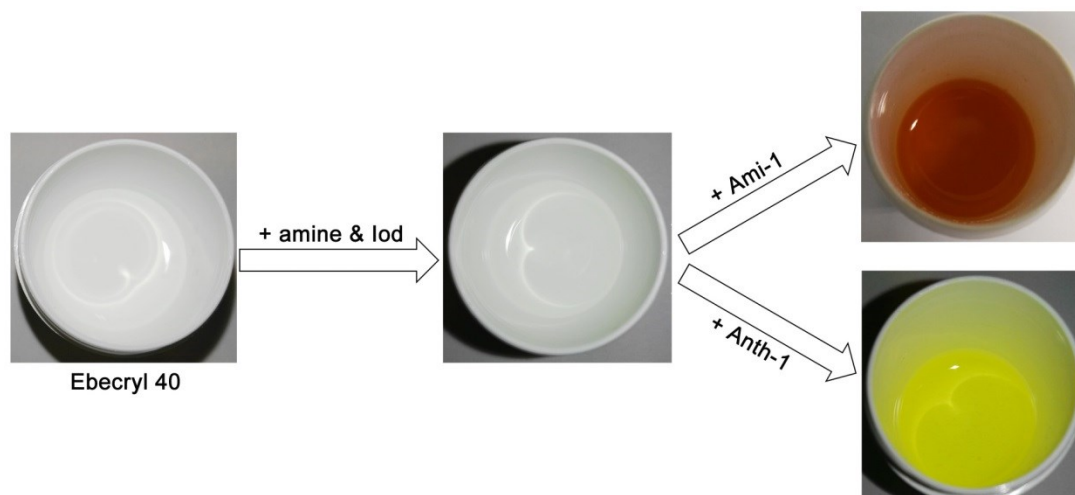
Chemical Formula: C<sub>42</sub>H<sub>31</sub>NO  
Molecular Weight: 565.7160

1-Benzylpiperidin-4-one (1.90 g, 10 mmol, M = 189.26 g/mol) and anthracene-9-carbaldehyde (4.12 g, 20 mmol, M = 206.24 g/mol) were dissolved in ethanol (50 mL) and aq. KOH (40%) (15 mL) was added. The solution was stirred at room temperature overnight. During reaction, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. The resulting solid was dissolved in dichloromethane and the solution was filtered on a plug of SiO<sub>2</sub> using dichloromethane as the eluent. The solvent was removed under reduced pressure. Dissolution in a minimum of dichloromethane followed by addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under vacuum (4.97g, 88% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.18 (s, 2H), 3.23 (s, 4H), 6.68 (d, 4H, J = 3.8 Hz), 6.82-6.85 (m, 1H), 7.49-7.51 (m, 8H), 8.01-8.08 (m, 8H), 8.44 (s, 2H), 8.75 (s, 2H); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ: 3.18 (s, 4H), 3.29 (s, 2H), 6.58 (t, 2H, J = 7.3 Hz), 6.64 (d, 2H, J = 6.9 Hz), 6.77 (t, 1H, J = 7.2 Hz), 7.57-7.64 (m, 8H), 8.07 (d, 4H, J = 8.3 Hz), 8.15 (d, 4H, J = 9.3 Hz), 8.58 (s, 2H), 8.69 (s, 2H); HRMS (ESI MS) m/z: theor: 564.2453 found: 564.2458 (M<sup>+</sup> detected); Anal. Calc. for C<sub>20</sub>H<sub>18</sub>FeO<sub>2</sub>: C, 91.5; H, 5.7; O, 2.8; Found: C, 91.4; H, 5.2; O, 3.0 %.

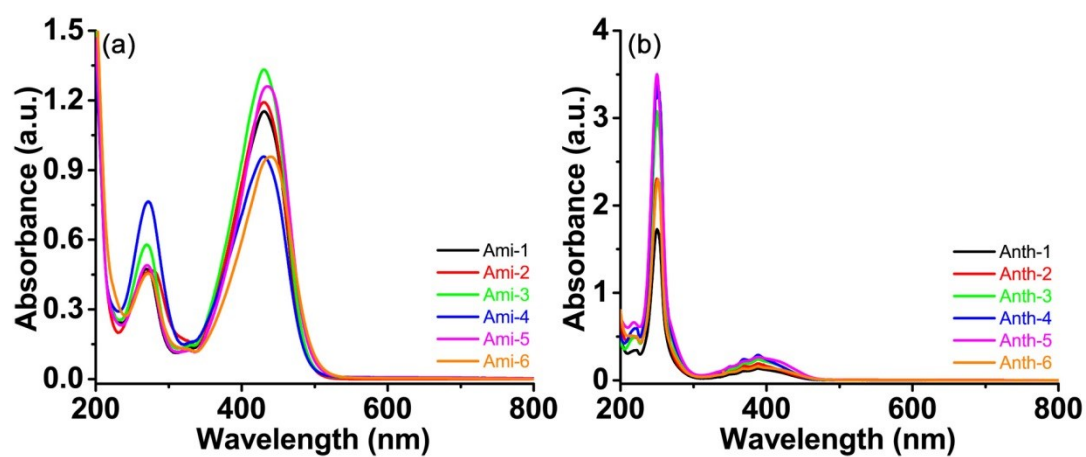


**Table S1.** Basic formulation for the free radical photopolymerization.

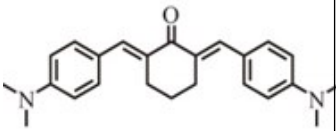


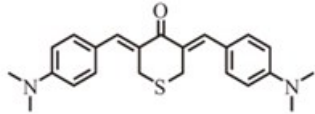


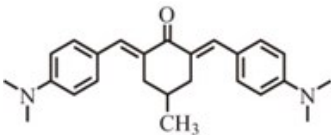


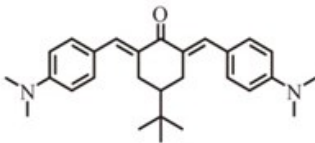
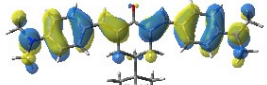
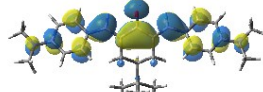
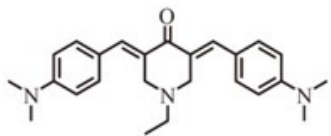


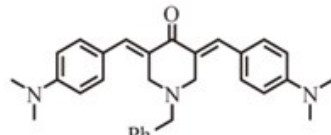
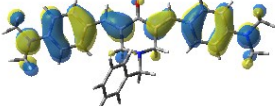

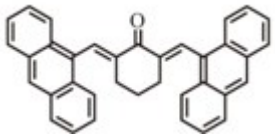
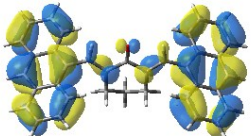

Ketone (0.1%, w)	amine (EDB) (2%, w)	Iod (Speedcure938) (2%, w)	TA (Ebecryl 40)
2.0 mg	40.0 mg	40.0 mg	2.0 g

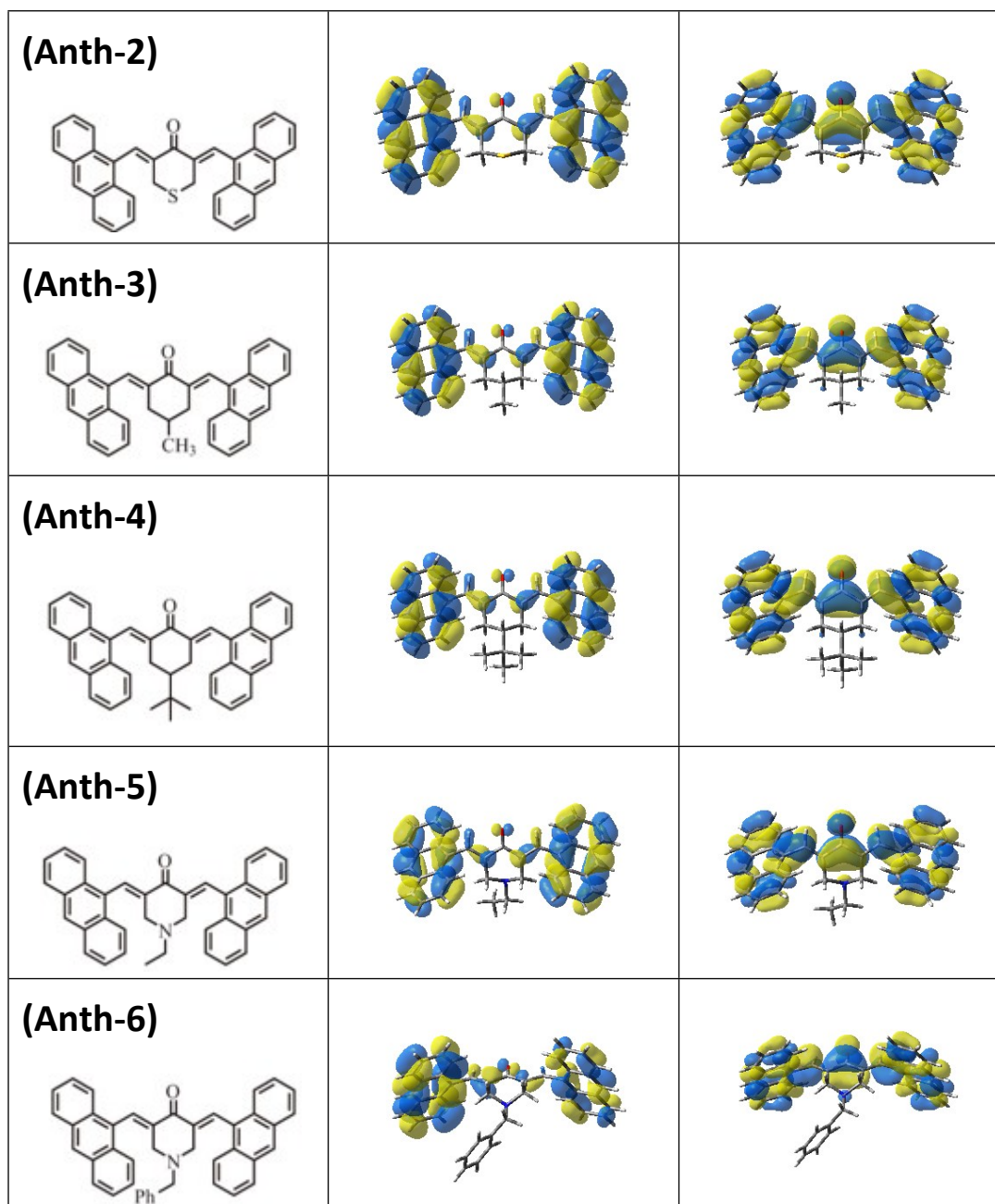


**Figure S1** *In situ* photograph for the preparation of the LED sensitive formulations.

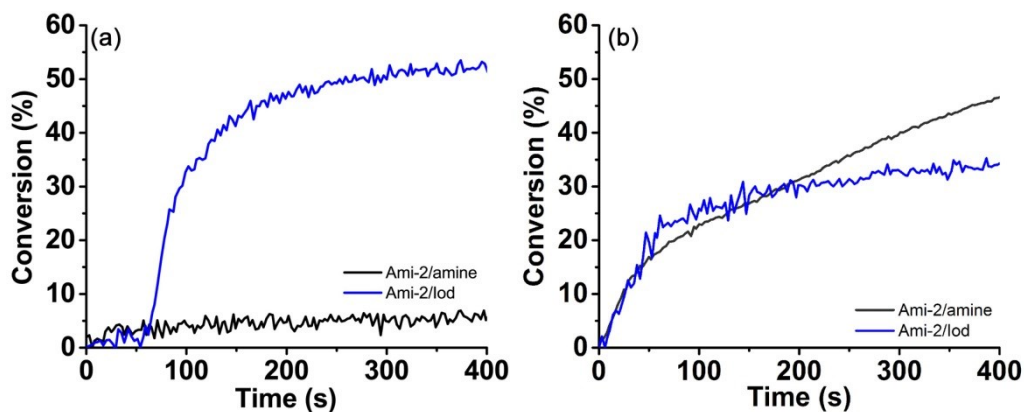


**Figure S2** UV-visible absorption spectra of the twelve ketone derivatives dissolved in acetonitrile (0.01 mg/mL).

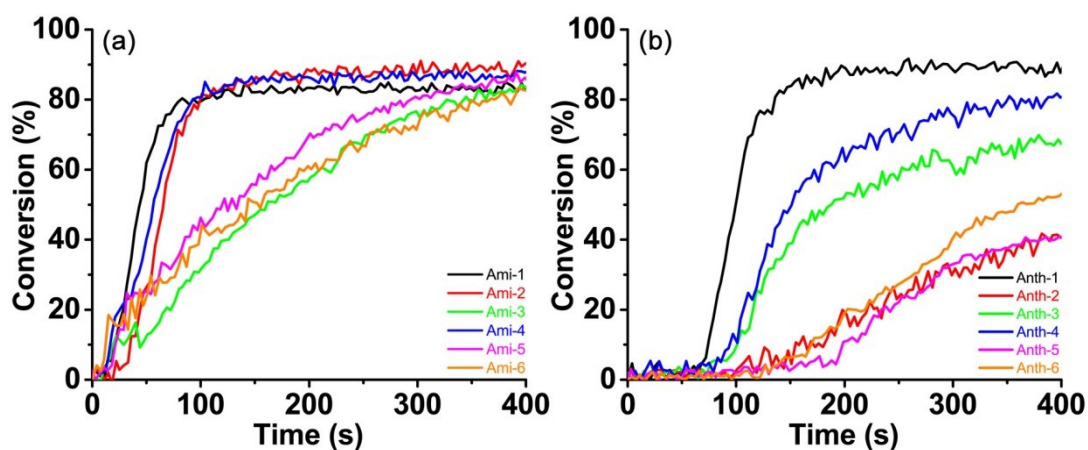
	HOMO	LUMO
<b>(Ami-1)</b> 		
<b>(Ami-2)</b> 		
<b>(Ami-3)</b> 		
<b>(Ami-4)</b> 		
<b>(Ami-5)</b> 		
<b>(Ami-6)</b> 		
<b>(Anth-1)</b> 		



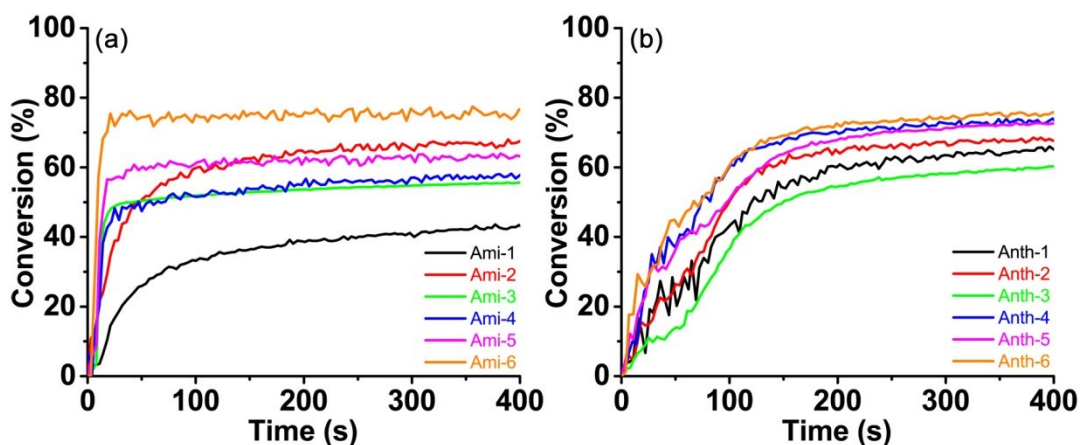
**Figure S3** Frontier molecular orbitals properties (HOMOs and LUMOs) of newly proposed ketones (calculated at UB3LYP/6-31G\* level – iso value=0.02).



**Figure S4** Photopolymerization profiles of TA (acrylate function conversion vs. irradiation time) in the presence of Ami-2/amine or Ami-2/Iod (0.1%/2%, w/w) two-component photoinitiating systems upon exposure to a LED@405 nm: (a) in thick films (thickness ≈ 1.4 mm) and (b) in thin films (thickness ≈ 25 μm), respectively.



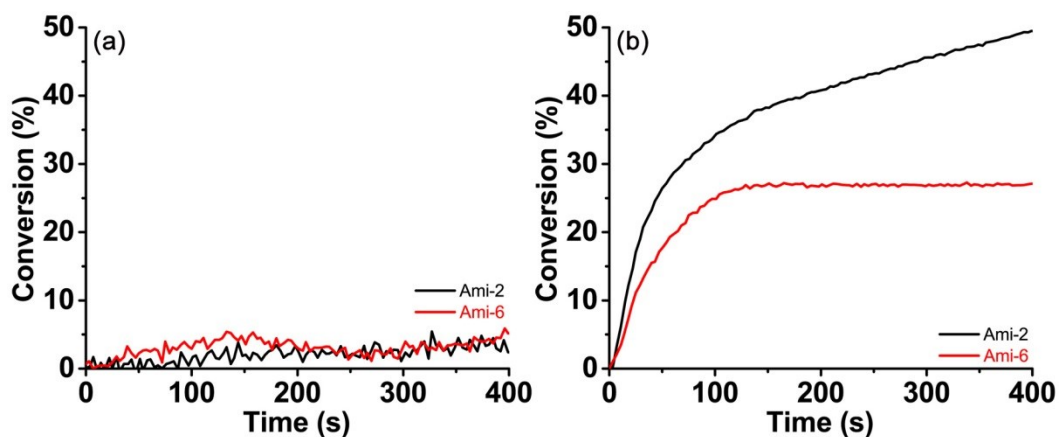
**Figure S5** Photopolymerization profiles of TA (acrylate function conversion vs. irradiation time) in thick films (thickness ≈ 1.4 mm) upon exposure to a LED@405 nm in the presence of ketone/amine/Iod (0.1%/2%/2%, w/w/w) three-component photoinitiating systems.



**Figure S6** Photopolymerization profiles of TA (acrylate function conversion vs. irradiation time) in thin films (thickness $\approx$ 25  $\mu$ m) upon exposure to a LED@405 nm in the presence of ketone/amine/Iod (0.1%/2%/2%, w/w/w) three-component photoinitiating systems.

**Table S2** Curve slopes of the photopolymerization profiles for reactive acrylates in thick and thin films conditions, respectively, upon exposure to LED@405 nm irradiation for 400 s in the presence of ketone/amine/Iod (0.1%/2%/2%, w/w/w) three-component photoinitiating systems.

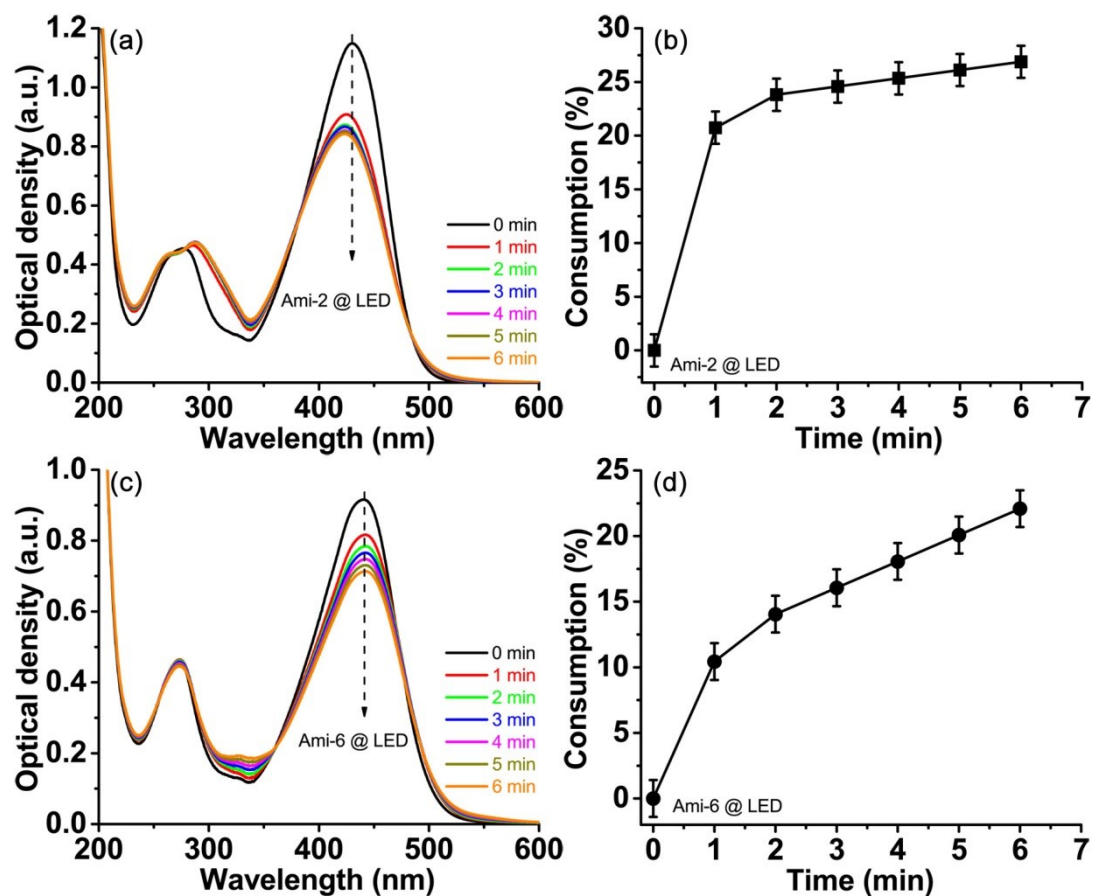
Slopes (in thick)	Ami-1	Ami-2	Ami-3	Ami-4	Ami-5	Ami-6
	$\sim$ 1.44	$\sim$ 1.36	$\sim$ 0.32	$\sim$ 1.39	$\sim$ 0.31	$\sim$ 0.28
	Anth-1	Anth-2	Anth-3	Anth-4	Anth-5	Anth-6
	$\sim$ 1.32	$\sim$ 0.14	$\sim$ 0.31	$\sim$ 0.54	$\sim$ 0.23	$\sim$ 0.21
Slopes (in thin)	Ami-1	Ami-2	Ami-3	Ami-4	Ami-5	Ami-6
	$\sim$ 0.45	$\sim$ 0.89	$\sim$ 2.47	$\sim$ 2.26	$\sim$ 3.47	$\sim$ 4.72
	Anth-1	Anth-2	Anth-3	Anth-4	Anth-5	Anth-6
	$\sim$ 0.38	$\sim$ 0.45	$\sim$ 0.38	$\sim$ 0.61	$\sim$ 0.44	$\sim$ 0.61



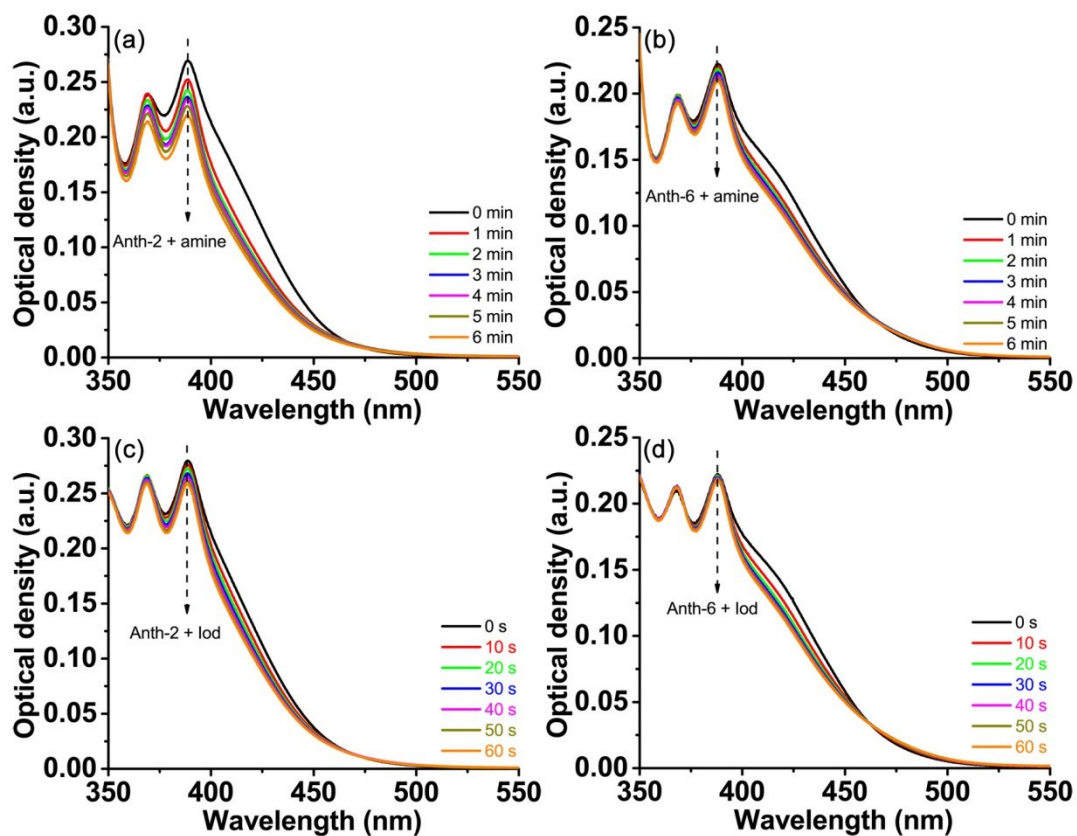
**Figure S7** Photopolymerization profiles of TA (acrylate function conversion vs. irradiation time) initiated by Ami-2 or Ami-6 (0.1%, w) in the absence of any photo-additives (EDB or Speedcure 938) upon exposure to LED@405 nm irradiation for 400 s: (a) in thick films (thickness $\approx$ 1.4 mm) and (b) in thin films (thickness $\approx$ 25  $\mu$ m), respectively.

**Table S3** Final conversions (FCs) for reactive acrylates of TA in thick and thin films conditions, respectively, upon exposure to LED@405 nm for 400 s in the presence of ketones alone without any photo-additives.

FCs (in thick)	Ami-2	Ami-6
	3%	5%
FCs (in thin)	Ami-2	Ami-6
	49%	27%



**Figure S8** Left: UV-vis absorption spectra of (a) Ami-2 ( $2.64 \times 10^{-5}$  M) and (c) Ami-6 ( $2.21 \times 10^{-5}$  M) alone in the solvent of acetonitrile upon exposure to LED@405 nm irradiation for 6 min. Right: Consumption of (b) Ami-2 and (d) Ami-6 vs. LED@405 nm irradiation time, respectively.



**Figure S9** Up: UV-vis absorption spectra of (a) Anth-2 ( $2.03 \times 10^{-5}$  M) and (b) Anth-6 ( $1.77 \times 10^{-5}$  M) in the presence of amine (EDB,  $1.03 \times 10^{-2}$  M) upon exposure to LED@405 nm irradiation for 6 min. Down: UV-vis absorption spectra of (c) Anth-2 ( $2.03 \times 10^{-5}$  M) and (d) Anth-6 ( $1.77 \times 10^{-5}$  M) in the presence of iodonium salt (Speedcure 938,  $1.03 \times 10^{-2}$  M) upon exposure to LED@405 nm irradiation for 60 s, respectively. The solvent is acetonitrile.