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Photoinitiator-Catalyst Systems Based on Meta-Terphenyl Derivatives as Photosensitisers of Iodonium and Thianthrenium Salts for Visible Photopolymerization in 3D Printing Processes

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1. Materials and experimental techniques

2-amino-4-(4-bromophenyl)-6-phenyl-benzene-1,3-dicarbonitrile for synthesis of all target compounds was synthesized following published procedure [1]. Unless otherwise noted, all organic compounds, inorganic salts and solvents were analytically pure and used as received. DMF was dried over molecular sieves.

Structure and purity of obtained products were confirmed by high field NMR. ¹H and ¹³CNMR spectra were recorded in CDCl₃ or DMSO-D₆ on Bruker Advance III 600 MHz spectrometer. Chemical shifts were reported in parts per million (δ) and referenced to residual protonated solvent peak (δ =7.26 ppm for CDCl₃ or δ =2.50 ppm for DMSO-D₆ in ¹HNMR spectra and 77.16 ppm for CDCl₃ in ¹³CNMR spectra). Melting points below 250 °C were determined with capillary melting-point apparatus and were uncorrected.

2. Synthetic procedures and physicochemical data of obtained compounds

2.1. 2-amino-4-phenyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile derivatives

General procedure for Suzuki coupling of 2-amino-4-(4-bromophenyl)-6-phenyl-benzene-1,3-dicarbonitrile



2-amino-4-(4-bromophenyl)-6-phenyl-benzene-1,3-dicarbonitrile (150 mg, 0.40 mmol), $Pd(OOCCH_3)_2$ (15 mg, 0.07 mmol), Na_2CO_3 2M solution (3.0 mL), appropriate phenylboronic acid derivative (0.80 mmol) and DMF (4.5 mL) were placed under nitrogen in the pressure vial and heated for 24 h at a temperature of 110 °C. Resulting mixture was treated with H_2O (15 mL) and extracted with $CHCI_3$ (3 × 15 mL). Organic extracts were combined, dried over anhydrous $MgSO_4$ and concentrated under vacuum. Products were purified by column chromatography (silica gel/CHCI₃) followed by crystallization from $CHCI_3$ /hexanes mixture.

Structure and purity of obtained 2-amino-4-phenyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile derivatives.

	Yield: 120 mg (81 %); m.p. 224 °C;	
TER-Ph-1	¹ H NMR (600 MHz, CDCl ₃) δ 7.75 – 7.72 (m, 2H), 7.70 – 7.67 (m,	
NH ₂	2H), 7.66 – 7.63 (m. 2H), 7.62 – 7.59 (m. 2H), 7.54 – 7.46 (m. 5H),	
NCCN	7.42 – 7.38 (m, 1H), 6.95 (s, 1H), 5.41 (s, 2H);	
	¹³ C NMR (101 MHz, DMSO) δ 154.2, 149.9, 149.4, 141.1, 139.2, 137.5, 136.4, 129.5, 129.2, 129.0, 128.7, 128.6, 128.05, 126. 9, 126.8, 118.59, 116.1, 116.0, 94.0, 93.9	
2-amino-4-phenyl-6-(4-phenylphenyl) benzene-1,3-dicarbonitrile	purity (LC): >94%; MS (ESI) m/z(%): 372 ([M+H]+, 100%).	

	Yield: 100 mg (63 %); m.p. 192°C;	
TER-Ph-2	¹ H NMR (400 MHz, DMSO) δ 8.01 – 7.90 (m, 6H), 7.83 – 7.77 (m, 2H), 7.68 – 7.63 (m, 2H), 7.57 – 7.50 (m, 3H), 6.90 – 6.82 (m, 3H);	
	¹³ C NMR (101 MHz, DMSO) δ 154.2, 149.9, 149.1, 143.6, 139.1, 137.7, 137.4, 132.9, 129.5, 129.4, 128.7, 128.68, 127.7, 127.3, 118.8, 118.5, 116.0, 116.0, 110.5, 94.2, 93.9.;	
2-amino-4-[4-(4-cyanophenyl)phenyl]-6- phenyl-benzene-1,3-dicarbonitrile	purity (LC): >95%; MS (ESI) m/z(%): 397 ([M+H]+, 100%), 369 ([M–HCN]+, 40%).	
	Yield: 110 mg (68 %); m.p. 213 °C;	
TER-Ph-3	^{1}H NMR (600 MHz, CDCl_3) δ 7.71 – 7.67 (m, 2H), 7.67 – 7.64 (m, 2H), 7.61 – 7.57 (m, 4H), 7.53 – 7.49 (m, 3H), 7.03 – 6.99 (m, 2H), 6.94 (s, 1H), 5.40 (s, 2H), 3.87 (s, 3H);	
	¹³ C NMR (101 MHz, DMSO) δ 159.3, 154.2, 149.8, 149.5, 140.8, 137.5, 135.6, 131.4, 129.4, 129.2, 128.7, 128.6, 127.9, 126.3, 118.4, 116.2, 116.1, 114.5, 93.9, 93.8;	
2-amino-4-[4-(4-methoxyphenyl)phenyl]-6- phenyl-benzene-1,3-dicarbonitrile	purity (LC): >99%; MS (ESI) m/z(%): 402 ([M+H]+, 100%).	
	Yield: 100 mg (57 %); m.p. 123 °C;	
TER-Ph-4 $\downarrow \downarrow $	^{1}H NMR (400 MHz, CDCl_3) δ 7.77 – 7.74 (m, 6H), 7.73 – 7.70 (m, 2H), 7.63 – 7.59 (m, 2H), 7.55 – 7.51 (m, 3H), 6.96 (s, 1H), 5.42 (s, 2H);	
	¹³ C NMR (101 MHz, DMSO) δ 154.2, 149.9, 149.1, 143.2, 139.5, 137.5, 137.4, 129.5, 129.4, 128.7, 128.6, 128.2 (q, <i>J</i> = 31.8 Hz), 127.6, 127.3, 125.9 (q, <i>J</i> = 3.7 Hz), 124.3 (q, <i>J</i> = 271.9 Hz), 118.5, 116.0, 116.0, 94.2, 93.9.;	
	purity (LC): >96%; MS (ESI) m/z(%): 440 ([M+H]+, 90%), 420 ([M–F]+, 80%), 400 ([M–2F–H]+, 100%).	
	Yield: 100 mg (60 %); m.p. 245 °C;	
TER-Ph-5 NC+++CN C++++CN C-amino-4-[4-(4- methylsulfanylphenyl)phenyl]-6-phenyl- benzene-1,3-dicarbonitrile	^1H NMR (600 MHz, CDCl_3+DMSO) δ 7.71 – 7.69 (m, 2H), 7.67 – 7.65 (m, 2H), 7.60 – 7.56 (m, 4H), 7.53 – 7.48 (m, 3H), 7.36 – 7.33 (m, 2H), 6.90 (s, 1H), 5.68 (s, 2H), 2.53 (s, 3H);	
	^{13}C NMR (101 MHz, DMSO) δ 154.2, 149.9, 149.4, 140.5, 138.3, 137.5, 136.2, 135.5, 129.5, 129.3, 128.7, 128.6, 127.2, 126.5, 126.3, 118.5, 116.1, 116.0, 94.0, 93.8, 14.5.;	
	purity (LC): >95%; MS (ESI) m/z(%): 419 ([M+H]+, 100%).	

	Viold: 100 mg (61 %); m n 101 °C;		
TER-Ph-6 $\downarrow \downarrow $	¹ H NMR (600 MHz, CDCl ₃) δ 7.70 – 7.65 (m, 4H), 7.62 – 7.58 (m,		
	4H), 7.54 – 7.49 (m, 3H), 7.19 – 7.14 (m, 2H), 6.94 (s, 1H), 5.41 (s, 2H);		
	¹³ C NMR (101 MHz, DMSO) δ 162.2 (d, $J = 245.1$ Hz), 154.2, 149.98, 149.3, 140.1, 137.5, 136.4, 135.6 (d, $J = 3.0$ Hz), 129.5, 129.2, 128.9, 128.8, 128.7, 128.6, 126.8, 118.5, 116.1 (d, $J = 6.6$ Hz), 115.9 (d, $J = 21.4$ Hz), 94.0, 93.9.		
	purity (LC): >97%; MS (ESI) m/z(%): 390 ([M+H]+, 100%).		
	Yield: 100 mg (65 %); m.p. 193 °C;		
TER-Ph-7 NC+++CN ++++CN +++++++++++++++++++++++	^{1}H NMR (400 MHz, CDCl_3) δ 7.74 – 7.70 (m, 2H), 7.68 – 7.64 (m, 2H), 7.61 – 7.58 (m, 2H), 7.56 – 7.53 (m, 2H), 7.52 – 7.49 (m, 3H), 7.31 – 7.27 (m, 2H), 6.95 (s, 1H), 5.40 (s, 2H), 2.42 (s, 3H);		
	^{13}C NMR (101 MHz, CDCl_3) δ 153.4, 150.2, 149.9, 142.7, 138.0, 137.6, 137.3, 136.0, 130.0, 129.8, 129.1, 129.0, 128.6, 127.5, 127.1, 120.2, 116.2, 116.1, 95.0, 94.9, 21.3.		
	purity (LC): >92%; MS (ESI) m/z(%): 386 ([M+H]+, 100%).		

¹HNMR spectra of 2-amino-4-phenyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile derivatives.



Figure S1: ¹HNMR spectrum of 2-amino-4-phenyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile, TER-Ph-1.



Figure S2: ¹HNMR spectrum of 2-amino-4-[4-(4-cyanophenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-Ph-2.



Figure S3: ¹HNMR spectrum of 2-amino-4-[4-(4-methoxyphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-Ph-3.



Figure S5: ¹HNMR spectrum of 2-amino-4-[4-(4-methylsulfanylphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-Ph-5.



Figure S6: ¹HNMR spectrum of 2-amino-4-[4-(4-fluorophenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-Ph-6.



Figure S7: ¹HNMR spectrum of 2-amino-4-[4-(4-methylphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-Ph-7.



Figure S9: ¹³CNMR spectrum of 2-amino-4-[4-(4-cyanophenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-Ph-2.



Figure S11: ¹³CNMR spectrum of 2-amino-4-phenyl-6-[4-[4-(trifluoromethyl)phenyl]phenyl]benzene-1,3-dicarbonitrile, TER-Ph-4.



Figure S13: ¹³CNMR spectrum of 2-amino-4-[4-(4-fluorophenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-Ph-6.



Figure S14: ¹³CNMR spectrum of 2-amino-4-[4-(4-methylphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-Ph-7.

2.2. 2-amino-4-phenyl-6-[4-[(E)-styryl]phenyl]benzene-1,3-dicarbonitrile derivatives

General procedure for Suzuki coupling of 2-amino-4-(4-bromophenyl)-6-phenyl-benzene-1,3-dicarbonitrile



2-amino-4-(4-bromophenyl)-6-phenyl-benzene-1,3-dicarbonitrile (150 mg, 0.40 mmol), Pd(OOCCH₃)₂ (7 mg, 0.03 mmol), triphenylphosphine (8 mg, 0.03 mmol), K₂CO₃ (145 mg, 1.00 mmol), appropriate styrene derivative (1.20 mmol) and anhydrous DMF (2 mL) were placed under nitrogen in the pressure vial and heated for 24 h at a temperature of 100 °C. Resulting mixture was treated with H₂O (10 mL) and extracted with CHCl₃ (3 × 10 mL). Organic extracts were combined, dried over anhydrous MgSO₄ and concentrated under vacuum. Products were purified by column chromatography (silica gel/CHCl₃) followed by crystallization from CHCl₃/hexanes mixture.

Structure and purity of obtained 2-amino-4-phenyl-6-[4-[(E)-styryl]phenyl]benzene-1,3-dicarbonitrile derivatives.

	Yield: 100 mg (63 %); m.p. 204 °C;		
TER-ST-1	¹ H NMR (400 MHz, DMSO) δ 7.79 – 7.74 (m, 2H), 7.70 – 7.62 (m, 6H), 7.57 – 7.51 (m, 3H), 7.44 – 7.36 (m, 4H), 7.32 – 7.27 (m, 1H), 6.88 – 6.80 (m, 3H);		
	¹³ C NMR (101 MHz, DMSO) δ 154.2, 149.8, 149.4, 138.3, 137.5, 136.8, 136.3, 129.9, 129.4, 129.0, 128.7, 128.7, 128.65, 128.0, 127.5, 126.7, 126.6, 118.4, 116.1, 116.0, 94.0, 93.8;		
2-amino-4-phenyl-6-[4-[€- styryl]phenyl]benzene-1,3-dicarbonitrile	purity (LC): >97%; MS (ESI) m/z(%): 398 ([M+H]+, 100%).		
	Yield: 104 mg (59%); m.p. 163 °C;		
TER-ST-2	¹ H NMR (400 MHz, DMSO) δ 8.30 – 8.23 (m, 2H), 7.94 – 7.89 (m, 2H), 7.87 – 7.80 (m, 2H), 7.75 – 7.69 (m, 2H), 7.67 – 7.51 (m, 7H), 6.92 – 6.81 (m, 3H);		
NO ₂	¹³ C NMR (101 MHz, DMSO) δ 154.2, 149. 9, 149.2, 146.4, 143.8, 137.5, 137.3, 132.3, 129.5, 129.2, 128.8, 128.7, 128.6, 127.8, 127.5, 127.3, 124.1, 118.4, 116.1, 116.0, 94.1, 93.8;		
2-amino-4-[4-[€-2-(4-nitrophenyl)vinyl]phenyl]- 6-phenyl-benzene-1,3-dicarbonitrile	purity (LC): >99%; MS (ESI) m/z(%): 441 ([M–H]+, 100%).		

	Yield: 120 mg (71%); m.p. 175 °C;
TER-ST-3 NC++CN CON 2-amino-4-[4-[(E)-2-(4- cyanophenyl)vinyl]phenyl]-6-phenyl- benzene-1,3-dicarbonitrile	¹ H NMR (400 MHz, DMSO) δ 7.89 – 7.77 (m, 6H), 7.73 – 7.67 (m, 2H), 7.67 – 7.62 (m, 2H), 7.58 – 7.52 (m, 4H), 7.48 (d, <i>J</i> = 16.5 Hz, 1H), 6.89 – 6.81 (m, 3H);
	¹³ C NMR (101 MHz, DMSO) δ 154.2, 149.9, 149.3, 141.6, 137.6, 137.5, 137.1, 132.6, 131.3, 129.4, 129.1, 128.7, 128.6, 128.2, 127.3, 127.2, 119.0, 118.4, 116.1, 116.0, 109.8, 94.1, 93.8;
	purity (LC): >90%; MS (ESI) m/z(%): 423 ([M+H]+, 100%).
	Yield: 82 mg (48%); m.p. 246 °C;
TER-ST-4 NC+++CN CON CON 2-amino-4-[4-[(E)-2-(4- methoxyphenyl)vinyl]phenyl]-6-phenyl- benzene-1,3-dicarbonitrile	¹ H NMR (400 MHz, DMSO) δ 7.74 – 7.69 (m, 2H), 7.68 – 7.62 (m, 4H), 7.60 – 7.56 (m, 2H), 7.56 – 7.50 (m, 3H), 7.34 (d, <i>J</i> = 16.4 Hz, 1H), 7.18 (d, <i>J</i> = 16.4 Hz, 1H), 7.00 – 6.94 (m, 2H), 6.84 (s, 1H), 6.81 (s, 2H), 3.79 (s, 3H).
	¹³ C NMR (101 MHz, DMSO) δ 159.2, 154.2, 149.8, 149.5, 138.7, 137.5, 135.8, 129.6, 129.5, 129.4, 129.0, 128.7, 128.6, 128.0, 126.3, 125.2, 118.4, 116.2, 116.1, 114.2, 93.9, 93.7, 55.2;
	purity (LC): >98%; MS (ESI) m/z(%): 428 ([M+H]+, 100%).
	Yield: 47 mg (26%); m.p. 238 °C;
TER-ST-5 NC+CR CN CN CN CN CN CN CN CN CN CN	¹ H NMR (400 MHz, DMSO) δ 7.77 – 7.71 (m, 2H), 7.68 – 7.63 (m, 4H), 7.61 – 7.56 (m, 2H), 7.56 – 7.51 (m, 3H), 7.36 (d, <i>J</i> = 16.4 Hz, 1H), 7.33 – 7.25 (m, 3H), 6.86 – 6.81 (m, 3H), 2.50 (s, 3H);
	¹³ C NMR (101 MHz, DMSO) δ 154.2, 149.8, 149.4, 138.4, 138.1, 137.5, 136.2, 133.5, 129.4, 129.4, 129.0, 128.7, 128. 6, 127.2, 126.7, 126.5, 126.0, 118.4, 116.1, 116.1, 93.9, 93.8, 14.6;
	purity (LC): >99%; MS (ESI) m/z(%): 444 ([M+H]⁺, 100%).
	Yield: 114 mg (69%); m.p. 254 °C;
TER-ST-6 NC+++CN CON 2-amino-4-[4-[(E)-2-(4- methylphenyl)vinyl]phenyl]-6-phenyl- benzene-1,3-dicarbonitrile	¹ H NMR (400 MHz, DMSO) δ 7.77 – 7.71 (m, 2H), 7.69 – 7.63 (m, 4H), 7.57 – 7.50 (m, 5H), 7.36 (d, <i>J</i> = 16.5 Hz, 1H), 7.27 (d, <i>J</i> = 16.5 Hz, 1H), 7.23 – 7.19 (m, 2H), 6.87 – 6.77 (m, 3H), 2.32 (s, 3H);
	¹³ C NMR (101 MHz, DMSO) δ 154.2, 149.8, 149.4, 138.5, 137.5, 137.4, 136.1, 134.1, 129.8, 129.4, 129.4, 129.0, 128.7, 128.6, 126.6, 126.5, 126.5, 118.4, 116.1, 116.1, 93.9, 93.8, 20.9.;
	purity (LC): >98%; MS (ESI) m/z(%): 412 ([M+H]+, 100%).

	Yield: 117 mg (68 %); m.p. 219 °C;
TER-ST-7 NH ² CN CI 2-amino-4-[4-[(E)-2-(4- chlorophenyl)vinyl]phenyl]-6-phenyl- benzene-1,3-dicarbonitrile	¹ H NMR (400 MHz, DMSO) δ 7.79 – 7.73 (m, 2H), 7.69 – 7.63 (m, 6H), 7.56 – 7.51 (m, 3H), 7.48 – 7.43 (m, 2H), 7.41 (d, <i>J</i> = 16.7 Hz, 1H), 7.36 (d, <i>J</i> = 16.5 Hz, 1H), 6.87 – 6.79 (m, 3H); ¹³ C NMR (101 MHz, DMSO) δ 154.2, 149.9, 149.4, 138.0, 137.5,
	136.5, 135.8, 132.2, 129.4, 129.0, 128.7, 128.7, 128.6, 128.5, 128.4, 128.3, 126.8, 118.4, 116.1, 116.0, 94.0, 93.8 purity (LC): >98%; MS (ESI) m/z(%): 433 ([M+H]+, 100%).
	Yield: 103 mg (62%); m.p. 189 °C;
TER-ST-8 $\downarrow \downarrow $	¹ H NMR (400 MHz, DMSO) δ 7.79 – 7.72 (m, 2H), 7.72 – 7.62 (m, 6H), 7.57 – 7.50 (m, 3H), 7.40 (d, <i>J</i> = 16.5 Hz, 1H), 7.30 (d, <i>J</i> = 16.5 Hz, 1H), 7.26 – 7.20 (m, 2H), 6.88 – 6.80 (m, 3H).
	¹³ C NMR (101 MHz, DMSO) δ 161.8 (d, $J = 245.2$ Hz), 154.2, 149.8, 149.4, 138.2, 137.5, 136.3, 133.4 (d, $J = 3.2$ Hz), 129.4, 129.0, 128.7, 128.6, 128.6, 128.5, 127.4 (d, $J = 2.2$ Hz), 126.6, 118.4, 116.1, 116.0, 115.6 (d, $J = 21.6$ Hz), 94.0, 93.8.;
	purity (LC): >98%; MS (ESI) m/z(%): 416 ([M+H]+, 100%).
	Yield: 145 mg (77%); m.p. 205 °C;
TER-ST-9 NC+++CN CON C-amino-4-[4-[(E)-2-(4-tert- butoxyphenyl)vinyl]phenyl]-6-phenyl-benzene- 1,3-dicarbonitrile	¹ H NMR (400 MHz, DMSO) δ 7.75 – 7.70 (m, 2H), 7.67 – 7.63 (m, 4H), 7.58 – 7.51 (m, 6H), 7.35 (d, <i>J</i> = 16.4 Hz, 1H), 7.22 (d, <i>J</i> = 16.4 Hz, 1H), 7.01 – 6.98 (m, 2H), 6.86 – 6.80 (m, 3H), 1.32 (s, 9H).
	¹³ C NMR (101 MHz, DMSO) δ 155.1, 154.2, 149.8, 149.5, 138.6, 137.5, 136.0, 131.7, 129.5, 129.4, 129.0, 128.7, 128.6, 127.4, 126.4, 126.2, 123.7, 118.4, 116.2, 116.1, 93.9, 93.8, 78.3, 28.6.;
	purity (LC): >99%; MS (ESI) m/z(%): 470 ([M+H]+, 100%), 414 ([M–C4H8]+, 63%).

¹HNMR spectra of 2-amino-4-phenyl-6-[4-[(E)-styryl]phenyl]benzene-1,3-dicarbonitrile derivatives.



Figure S16: ¹HNMR spectrum of 2-amino-4-[4-[(E)-2-(4-nitrophenyl)vinyl]phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-ST-2.



Figure S17: ¹HNMR spectrum of 2-amino-4-[4-[(E)-2-(4-cyanophenyl)vinyl]phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-ST-3.



Figure S18: ¹HNMR spectrum of 2-amino-4-[4-[(E)-2-(4-methoxyphenyl)vinyl]phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-ST-4.



Figure S19: ¹HNMR spectrum of 2-amino-4-[4-[(E)-2-(4-methylsulfanylphenyl)vinyl]phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-ST-5.



Figure S20: ¹HNMR spectrum of 2-amino-4-[4-[(E)-2-(4-methylphenyl)vinyl]phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-ST-6.



Figure S21: ¹HNMR spectrum of 2-amino-4-[4-[(E)-2-(4-chlorophenyl)vinyl]phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-ST-7.



Figure S22: ¹HNMR spectrum of 2-amino-4-[4-[(E)-2-(4-fluorophenyl)vinyl]phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-ST-8.



Figure S23: ¹HNMR spectrum of 2-amino-4-[4-[(E)-2-(4-tert-butoxyphenyl)vinyl]phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-ST-9.



Figure S24: ¹³CNMR spectrum of 2-amino-4-phenyl-6-[4-[(E)-styryl]phenyl]benzene-1,3-dicarbonitrile, TER-ST-1.





Figure S28: ¹³CNMR spectrum of 2-amino-4-[4-[(E)-2-(4-methylsulfanylphenyl)vinyl]phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-ST-5.



Figure S30: ¹³CNMR spectrum of 2-amino-4-[4-[(E)-2-(4-chlorophenyl)vinyl]phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-ST-7.



Figure S32: ¹³CNMR spectrum of 2-amino-4-[4-[(E)-2-(4-tert-butoxyphenyl)vinyl]phenyl]-6-phenyl-benzene-1,3-dicarbonitrile, TER-ST-9.







Figure S34: UV-visible absorption spectra of investigated initiators: HIP and TT in acetonitrile.

3. Cyclic voltammetry curves showing oxidation and reduction processes of 2-amino-4-phenyl-6benzene-1,3-dicarbonitrile derivatives in acetonitrile



3.1. Cyclic voltammetry curves showing oxidation and reduction processes of 2-amino-4-phenyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile derivatives in acetonitrile.







3.2. Cyclic voltammetry curves showing oxidation and reduction processes of 2-amino-4-phenyl-6-[4-[(E)-styryl]phenyl]benzene-1,3-dicarbonitrile and derivatives in acetonitrile.





4.1. Examples of ESR spin trapping (ESR-ST) experiments for investigated of 2-amino-4-phenyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile derivatives in acetonitrile.



Figure S67: ESR spectra of the radicals generated by bimolecular photoinitiating system based on TER-Ph-2 and iodonium salt (HIP) exposure at room temperature under nitrogen upon UV-LED 365 nm irradiation and trapped by PBN in tert-butylbenzene: (black line) experimental and (red line) simulated spectra.

The simulation give the following hfc constants for the PBN spin adducts: aN = 14.4 G; aH = 2.2 G; % = 100.0 phenyl radical.



Magnetic field (G)

Figure S68: ESR spectra of the radicals generated by bimolecular photoinitiating system based on TER-Ph-7 and iodonium salt (HIP) exposure at room temperature under nitrogen upon UV-LED 365 nm irradiation and trapped by PBN in tert-butylbenzene: (black line) experimental and (red line) simulated spectra.

The simulation give the following hfc constants for the PBN spin adducts: aN = 14.4 G; aH = 2.2 G; % = 100.0 phenyl radical.

experimental

simulated



4.2. Examples of ESR spin trapping (ESR-ST) experiments for investigated of 2-amino-4-phenyl-6-[4-[(E)-styryl]phenyl]benzene-1,3-dicarbonitrile derivatives in acetonitrile.

40

20

0

-20

-40

3460

Figure S69: ESR spectra of the radicals generated by bimolecular photoinitiating system based on TER-ST-3 and iodonium salt (HIP) exposure at room temperature under nitrogen upon UV-LED 365 nm irradiation and trapped by PBN in tert-butylbenzene: (black line) experimental and

3470

PBN in tert-butylbenzene: (black line) experimental and (red line) simulated spectra. The simulation give the following hfc constants for the PBN spin adducts: aN = 14.3 G; aH = 2.2 G; % = 100.0

phenyl radical.



3480

3490

Magnetic field (G)

3500

3510

5. Spectroscopic properties - excitation and emission spectra.

5.1. Excitation and emission spectra for the determination of the excited singlet state energy for investigated of 2-amino-4-phenyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile derivatives in acetonitrile.



Figure S71: Excitation and emission spectra for the determination of the excited singlet state energy for TER-



Figure S73: Excitation and emission spectra for the determination of the excited singlet state energy for TER-



Figure S75: Excitation and emission spectra for the determination of the excited singlet state energy for TER-Ph-5 derivative.



Figure S72: Excitation and emission spectra for the determination of the excited singlet state energy for TER-Ph-2 derivative.



Figure S74: Excitation and emission spectra for the determination of the excited singlet state energy for TER-Ph-4derivative.







5.2. Excitation and emission spectra for the determination of the excited singlet state energy for investigated of 2-amino-4-phenyl-6-[4-[(E)-styryl]phenyl]benzene-1,3-dicarbonitrile derivatives in acetonitrile.



Figure S78: Excitation and emission spectra for the determination of the excited singlet state energy for TER-ST-1 derivative.



Figure S80: Excitation and emission spectra for the determination of the excited singlet state energy for TER-ST-3 derivative.



Figure S82: Excitation and emission spectra for the determination of the excited singlet state energy for TER-ST-5 derivative.



Figure S79: Excitation and emission spectra for the determination of the excited singlet state energy for TER-ST-2 derivative.



Figure S81: Excitation and emission spectra for the determination of the excited singlet state energy for TER-ST-4 derivative.



Figure S83: Excitation and emission spectra for the determination of the excited singlet state energy for TER-ST-6 derivative.



Figure S84: Excitation and emission spectra for the determination of the excited singlet state energy for TER-





Figure S85: Excitation and emission spectra for the determination of the excited singlet state energy for TER-ST-8 derivative.

6. Fluorescence quenching experiments with iodonium and thianthrenium salts







6.1. Fluorescence quenching with iodonium salt (IOD=HIP) of investigated 2-amino-4-phenyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile derivatives and with Stern-Volmer correlation





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Figure S89: Fluorescence quenching of TER-Ph-2.



Figure S91: Fluorescence quenching of TER-Ph-7.





Figure S92: Stern-Volmer plots for the fluorescence quenching of TER-Ph-7 by HIP. Solvent acetonitrile.

6.2. Fluorescence quenching with iodonium salt (IOD=HIP) of investigated 2-amino-4-phenyl-6-[4-[(E)-styryl]phenyl]benzene-1,3-dicarbonitrile derivatives and Stern-Volmer correlation



Figure S93: Fluorescence quenching of TER-ST-1.



Figure S94: Stern-Volmer plots for the fluorescence quenching of TER-ST-1 by HIP. Solvent acetonitrile.











Figure S96: Stern-Volmer plots for the fluorescence quenching of TER-ST-4 by HIP. Solvent acetonitrile.



Figure S98: Stern-Volmer plots for the fluorescence quenching of TER-ST-8 by HIP. Solvent acetonitrile.





Figure S99: Fluorescence quenching of TER-ST-4.



Figure S100: Stern-Volmer plots for the fluorescence quenching of TER-ST-4 by thianthrenium salt (TT). Solvent acetonitrile.



Figure S101: Fluorescence quenching of TER-ST-5.



Figure S103: Fluorescence quenching of TER-ST-6.



Figure S105: Fluorescence quenching of TER-ST-9.



Figure S102: Stern-Volmer plots for the fluorescence quenching of TER-ST-5 by thianthrenium salt (TT). Solvent acetonitrile.



Figure S104: Stern-Volmer plots for the fluorescence quenching of TER-ST-6 by thianthrenium salt (TT). Solvent acetonitrile.



Figure S106: Stern-Volmer plots for the fluorescence quenching of TER-ST-9 by thianthrenium salt (TT). Solvent acetonitrile.





Figure S107: Stern-Volmer plots for the fluorescence quenching of TER-ST-4 by HIP or TT. Solvent acetonitrile.



Figure S109: Stern-Volmer plots for the fluorescence quenching of TER-ST-6 by HIP or TT. Solvent acetonitrile.





7. Examples of steady state photolysis.

7.1. Examples of steady state photolysis upon exposure with LED @375nm for 2-amino-4-phenyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile derivatives and with iodonium salt (HIP) in acetonitrile



7.2. Examples of steady state photolysis upon exposure with LED @375nm for 2-amino-4-phenyl-6-[4-[(E)-styryl]phenyl]benzene-1,3-dicarbonitrile derivatives and with iodonium salt (HIP) in acetonitrile



7.3. Steady state photolysis upon exposure with LED @375nm for 2-amino-4-phenyl-6-[4-[(E)-styryl]phenyl]benzene-1,3-dicarbonitrile derivatives and with thianthrenium salt (TT) in acetonitrile



Figure S117: Photolysis of TER-ST-6 in ACN under 375nm (190mW/cm²).



Figure S118: Photolysis of TER-ST-6 + TT (concentration: 1,59·10⁻³ [mol/dm³]) in ACN under 375nm (190mW/cm²).

8. Lifetime of 2-amino-4-phenyl-6-benzene-1,3-dicarbonitrile and derivatives in acetonitrile.



8.1.Lifetime of 2-amino-4-phenyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile derivatives in acetonitrile

Figure S119: Fluorescence lifetime decay curves of TER-Ph-1 derivative with excitation pulse at 320 nm in ACN.



Figure S121: Fluorescence lifetime decay curves of TER-Ph-3 derivative with excitation pulse at 320 nm in ACN.







Figure S122: Fluorescence lifetime decay curves of TER-Ph-4 derivative with excitation pulse at 320 nm in ACN.





Figure S123: Fluorescence lifetime decay curves of TER-Ph-5 derivative with excitation pulse at 320 nm in ACN.



Figure S125: Fluorescence lifetime decay curves of TER-Ph-7 derivative with excitation pulse at 320 nm in ACN.

Figure S124: Fluorescence lifetime decay curves of TER-Ph-6 derivative with excitation pulse at 320 nm in ACN.



8.2. Lifetime of 2-amino-4-phenyl-6-[4-[(E)-styryl]phenyl]benzene-1,3-dicarbonitrile derivatives iin acetonitrile









Figure S130: Fluorescence lifetime decay curves of TER-ST-5 derivative with excitation pulse at 320 nm in ACN.



Figure S127: Fluorescence lifetime decay curves of TER-ST-2 derivative with excitation pulse at 320 nm in





TER-ST-4 derivative with excitation pulse at 320 nm in



Figure S131: Fluorescence lifetime decay curves of TER-ST-6 derivative with excitation pulse at 320 nm in ACN.



Figure S132: Fluorescence lifetime decay curves of TER-ST-7 derivative with excitation pulse at 320 nm in



Figure S134: Fluorescence lifetime decay curves of TER-ST-9 derivative with excitation pulse at 320 nm in ACN.



Figure S133: Fluorescence lifetime decay curves of TER-ST-8 derivative with excitation pulse at 320 nm in ACN.

9. The optimized structures and HOMO and LUMO orbitals of investigated compounds free molecules determined with the use of uB3LYP/6-31G* level of theory

Method uB3LYP/6-31G*	HOMO (Isoval = 0.02)	LUMO (Isoval = 0.02)		
For 2-amino-4-phenyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile derivatives				
TER-Ph-1 NC+CN CN 2-amino-4-phenyl-6-(4-phenylphenyl) benzene-1,3-dicarbonitrile				
TER-Ph-2 NC CN 2-amino-4-[4-(4-cyanophenyl)phenyl]-6- phenyl-benzene-1.3-dicarbonitrile				
TER-Ph-3 NC CN CN CN CN CN CN CN CN CN CN		من م		
Phenyl-benzene-1,3-dicarbonitrile TER-Ph-4 NC NC CN CF ₃ 2-amino-4-phenyl-6-[4-[4- (trifluoromethyl)phenyl]phenyl]benzene- 1,3-dicarbonitrile				
TER-Ph-5 NC+CN 2-amino-4-[4-(4- methylsulfanylphenyl)phenyl]-6-phenyl- benzene-1,3-dicarbonitrile				



10. Photopolymerization profiles (double bond function conversion vs. irradiation time) in the presence of different two and three component photoinitiating systems

10.1. Photopolymerization profiles (double bond function conversion vs. irradiation time) in the presence of type II initiating system containing meta-terphenyl derivatives and different amines as co-initiators



Figure S135: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type II photoinitating system based on amine (EDB, MDEA, TEAD) (1.5 % wt.) and TER-Ph-2 derivative (0,3% wt.) under irradiation at 365 nm



Figure S136: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type II photoinitating system based on amine (EDB, MDEA, TEAD) (1.5 % wt.) and TER-Ph-2 derivative (0,3% wt.) under irradiation at 405 nm



Figure S137: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type II photoinitating system based on amine (EDB, MDEA, TEAD) (1.5 % wt.) and TER-ST-2 derivative (0,3% wt.) under irradiation at 365 nm



Figure S139: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type II photoinitating system based on amine (EDB, MDEA, TEAD) (1.5 % wt.) and TER-ST-3 derivative (0,3% wt.) under irradiation at 365 nm



Figure S138: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type II photoinitating system based on amine (EDB, MDEA, TEAD) (1.5 % wt.) and TER-ST-2 derivative (0,3% wt.) under irradiation at 365 nm



Figure S140: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type II photoinitating system based on amine (EDB, MDEA, TEAD) (1.5 % wt.) and TER-ST-3 derivative (0,3% wt.) under irradiation at 365 nm





Figure S141: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine EDB (1.5 % wt.), Speedcure 938 (1 % wt.) and TER-Ph-2 derivative (0,3% wt.) under irradiation at 365 nm



Figure S143: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine MDEA (1.5 % wt.), Speedcure 938 (1 % wt.) and TER-Ph-2 derivative (0,3% wt.) under irradiation at 365 nm



Figure S142: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine EDB (1.5 % wt.), Speedcure 938 (1 % wt.) and TER-Ph-2 derivative (0.3% wt.) under irradiation at 405 nm



Figure S144: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine MDEA (1.5 % wt.), Speedcure 938 (1 % wt.) and TER-Ph-2 derivative (0,3% wt.) under irradiation at 405 nm



Figure S145: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine TEAD (1.5 % wt.), Speedcure 938 (1 % wt.) and TER-Ph-2 derivative (0,3% wt.) under irradiation at 365 nm



Figure S147: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine EDB (1.5 % wt.), Speedcure 938 (1 % wt.) and

TER-ST-2 derivative (0,3% wt.) under irradiation at 365 nm



Figure S146: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine TEAD (1.5 % wt.), Speedcure 938 (1 % wt.) and TER-Ph-2 derivative (0,3% wt.) under irradiation at 405 nm



Figure S148: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine EDB (1.5 % wt.), Speedcure 938 (1 % wt.) and TER-ST-2 derivative (0,3% wt.) under irradiation at 405 nm



Figure S149: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine MDEA (1.5 % wt.), Speedcure 938 (1 % wt.) and







Figure S150: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine MDEA (1.5 % wt.), Speedcure 938 (1 % wt.) and





Figure S152: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine TEAD (1.5 % wt.), Speedcure 938 (1 % wt.) and TER-ST-2 derivative (0,3% wt.) under irradiation at 405 nm



Figure S153: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine EDB (1.5 % wt.), Speedcure 938 (1 % wt.) and

TER-ST-3 derivative (0,3% wt.) under irradiation at 365 nm



Figure S155: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine MDEA (1.5 % wt.), Speedcure 938 (1 % wt.) and TER-ST-3 derivative (0,3% wt.) under irradiation at 365 nm



Figure S154: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine EDB (1.5 % wt.), Speedcure 938 (1 % wt.) and TER-ST-3 derivative (0,3% wt.) under irradiation at 405 nm



Figure S156: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine MDEA (1.5 % wt.), Speedcure 938 (1 % wt.) and TER-ST-3 derivative (0,3% wt.) under irradiation at 405 nm



Figure S157: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine TEAD (1.5 % wt.), Speedcure 938 (1 % wt.) and TER-ST-3 derivative (0,3% wt.) under irradiation at 365 nm



Figure S158: Free-radical photopolymerization profiles (acrylate function conversion vs. irradiation time) for TMPTA with type three-component photoinitiating system based on amine TEAD (1.5 % wt.), Speedcure 938 (1 % wt.) and TER-ST-3 derivative (0,3% wt.) under irradiation at 405 nm

10.3. Photopolymerization profiles for different reactions



Figure S159. (a) Cationic photopolymerization profiles (epoxy function conversion vs. irradiation time) initiated by bimolecular photoinitiating system based on HIP (1% wt.) and 2-amino-4-phenyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile derivatives (0.3% wt.) under irradiation atb(a) 365 nm (b) 405 nm. The measurements were carried out using Eq-1-IR.



Figure S160. (a) Cationic photopolymerization profiles (epoxy function conversion vs. irradiation time) initiated by bimolecular photoinitiating system based on HIP (1% wt.) and 2-amino-4-phenyl-6-[4-[(E)-styryl]phenyl]benzene-1,3-dicarbonitrile derivatives (0.3% wt.) under irradiation atb(a) 365 nm (b) 405 nm. The measurements were carried out using Eq-1-IR.



Figure S161. (a) Free-radical photopolymerization profiles (double bond conversion vs. irradiation time) initiated by bimolecular photoinitiating system based on HIP (1% wt.) and 2-amino-4-phenyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile derivatives (0.3% wt.) under irradiation atb(a) 365 nm (b) 405 nm. The measurements were carried out using Eq-1-IR.



Figure S162: (a) Free-radical photopolymerization profiles (double bond conversion vs. irradiation time) initiated by bimolecular photoinitiating system based on HIP (1% wt.) and 2-amino-4-phenyl-6-[4-[(E)-styryl]phenyl]benzene-1,3-dicarbonitrile derivatives (0.3% wt.) under irradiation atb(a) 365 nm (b) 405 nm. The measurements were carried out using Eq-1-IR.

11. 3D printed materials with the use of terphenyl derivatives as photosensitisers

It was shown that three-component systems are more efficient than two-component systems, they are both highly productive for 3D printing. It was confirmed by a 3D printing experiment for two and three component systems, under the same measurement conditions and the final printouts were qualitatively equal. Below we enclose photographs showing 3D printouts obtained under the same measurement conditions using a two and three-component initiation systems.



Figure S163. Hybrid photopolymerization of mixture: CADE/TMPTA (50/50 %w/w) with two-component photoinitiating system (2COMP) and three-component photoinitiating system (3COMP).
 Photoinitiating system - 2COMP: TER-ST-5 (0.3 % w/w) with iodonium salt (Speedcure 938, 1 %w/w) Photoinitiating system - 3COMP: TER-ST-5 (0.3 %w/w) with iodonium salt (Speedcure 938, 1 %w/w) with EDB (1.5 %w/w).