Supplementary material

The applicability of 2-amino-4,6-diphenyl-pyridine-3-carbonitrile sensors for monitoring different types of photopolymerization processes and acceleration of cationic and free-radical photopolymerization under near UV light

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1. Preparation and characterization of 2-amino-4,6-diphenyl-pyridine-3-carbonitrile derivatives

Derivatives of 2-amino-4,6-diphenylpyridine-3-carbonitrile were synthesized by modified protocol by Kambe et al. [48]. This procedure involved condensation reaction between earlier synthesized 2-benzylidenepropanedinitrile derivative and commercially available acetophenone.

![Chemical reaction diagram]

1.1. Materials and methods

Reagents for synthesis were purchased from Sigma-Aldrich or Alfa Aesar and used without further purification.

Structure and purity of obtained products were confirmed by NMR and LC-MS analysis. $^1$H NMR spectra were recorded in DMSO-D$_6$ on Avance III HD 400 MHz (Bruker) spectrometer. Chemical shifts are reported in parts per million (δ) and referenced to residual protonated solvent peak (δ = 2.50 ppm). LC-MS analyses were obtained on Shimadzu LCMS-2020 with ESI ionization method. Acetonitrile was used as eluent.

1.2. Synthesis of 2-benzylidenepropanedinitrile derivatives

The solution of sodium hydroxide (0.5 mmol, 20 mg) in water (5.0 cm$^3$) was added dropwise to mixed solution of appropriate benzaldehyde derivative (10.0 mmol) and malononitrile (12.0 mmol, 793 mg) in methanol (30.0 cm$^3$). After 30 minutes of stirring the resulting crystal-like precipitate was filtered under reduced pressure and dried under vacuum.

2-benzylidenepropanedinitrile,
10.00 g, yield: 65%,
$^1$H NMR (400 MHz, DMSO) δ 8.56 (s, 1H), 7.99 – 7.92 (m, 2H), 7.73 – 7.66 (m, 1H), 7.66 – 7.59 (m, 2H).
1.3. Synthesis of 2-amino-4,6-diphenylpyridine-3-carbonitrile derivatives

Ammonium acetate (7.10 mmol, 547 mg) was added to mixed solution of appropriate derivatives of acetophenone (6.50 mmol) and 2-benzylidenepropanedinitrile (6.50 mmol) in toluene (10.0 cm³). Resulting mixture was heated for 4 hours in temperature 100°C. Obtained solution was washed with water and saline, dried over anhydrous magnesium sulphate and concentrated under reduced pressure. Product with satisfying purity was obtained after crystallization from methanol.

2-amino-4,6-diphenylpyridine-3-carbonitrile (PHT20-002);
0.698 g Yield: 33%;
purity (LC): >99%;
1H NMR (400 MHz, DMSO) δ 8.17 – 8.10 (m, 2H), 7.72 – 7.65 (m, 2H), 7.60 – 7.53 (m, 3H), 7.52 – 7.46 (m, 3H), 7.28 (s, 1H), 7.02 (brs, 2H);
MS (ESI) m/z(%): 272 ([M+H]^+) 28%, 313 ([M+CH₃CN]^+ 100%).

2-amino-4-(4-cyanophenyl)-6-(4-methoxyphenyl)pyridine-3-carbonitrile (P64);
0.730 g, yield: 30%;
purity (LC): 95%;
1H NMR (400 MHz, DMSO) δ 8.15 – 8.09 (m, 2H), 8.07 – 8.01 (m, 2H), 7.90 – 7.84 (m, 2H), 7.27 (s, 1H), 7.09 – 7.01 (m, 4H), 3.82 (s, 3H);
MS (ESI) m/z(%): 327 ([M+H]^+ 19%), 368 ([M+CH₃CN]^+ 100%).
2-amino-6-(4-cyanophenyl)-4-(4-methoxyphenyl)pyridine-3-carbonitrile (P65);
0.370 g, yield: 15%;
purity (LC): 94%;
$^1$H NMR (400 MHz, DMSO) $\delta$ 8.34 – 8.28 (m, 2H), 8.00 – 7.93 (m, 2H), 7.71 – 7.65 (m, 2H), 7.38 (s, 1H), 7.14 – 7.10 (m, 2H), 7.08 (brs, 2H), 3.84 (s, 3H);
MS (ESI) m/z(%): 327 ([M+H]$^+$,10%), 368 ([M+CH$_3$CN]$^+$, 100%)

2-amino-4-(4-methoxyphenyl)-6-phenylpyridine-3-carbonitrile (P58);
0.630 g, yield: 27%;
purity (LC): >99%;
$^1$H NMR (400 MHz, DMSO) $\delta$ 8.15 – 8.09 (m, 2H), 7.70 – 7.63 (m, 2H), 7.53 – 7.44 (m, 3H), 7.25 (s, 1H), 7.14 – 7.08 (m, 2H), 6.95 (brs, 2H), 3.84 (s, 3H);
MS (ESI) m/z(%): 302 ([M+H]$^+$,64%), 343 ([M+CH$_3$CN]$^+$, 100%).

2-amino-6-(4-methoxyphenyl)-4-phenylpyridine-3-carbonitrile (P59);
0.790 g, yield: 34%;
purity (LC): >99%;
$^1$H NMR (400 MHz, DMSO) $\delta$ 8.15 – 8.09 (m, 2H), 7.70 – 7.63 (m, 2H), 7.58 – 7.50 (m, 3H), 7.22 (s, 1H), 7.07 – 7.00 (m, 2H), 6.94 (brs, 2H), 3.82 (s, 3H);
MS (ESI) m/z(%): 302 ([M+H]$^+$,62%), 343 ([M+CH$_3$CN]$^+$, 100%).

2-amino-4,6-bis(4-methoxyphenyl)pyridine-3-carbonitrile (P60);
0.800 g, yield: 32%;
purity (LC): >99%;
$^1$H NMR (400 MHz, DMSO) $\delta$ 8.14 – 8.06 (m, 2H), 7.68 – 7.61 (m, 2H), 7.19 (s, 1H), 7.14 – 7.07 (m, 2H), 7.06 – 7.00 (m, 2H), 6.87 (brs, 2H), 3.84 (s, 3H), 3.82 (s, 3H);
MS (ESI) m/z(%): 332 ([M+H]$^+$,74%), 373 ([M+CH$_3$CN]$^+$, 100%).
2. $^1$HNMR spectra of 2-amino-4,6-diphenylpyridine-3-carbonitrile derivatives

![HNMR spectra of 2-amino-4,6-diphenylpyridine-3-carbonitrile derivatives]
3. Materials for photopolymerization processes

3.1. Cationic photopolymerization under UV light with $\lambda_{\text{max}} = 320$ nm and under $\lambda_{\text{max}} = 365$ nm respectively.

3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CADE, from Allnex) as a cycloaliphatic epoxide monomer was used for the compositions cured by ring opening cationic photopolymerization. Triethylene glycol divinyl ether (TEGDVE, from Sigma Aldrich) was applied as a model vinyl ether monomer for cationic chain photopolymerization. For the role of cationic photoinitiator the diphenyliodonium hexafluorophosphate (HIP, from Alfa Aesar) was used under UV light with $\lambda_{\text{max}} = 320$ nm. The bimolecular photoinitiating systems based on diphenyliodonium hexafluorophosphate (HIP) and 2-amino-4,6-diphenyl-pyridine-3-carbonitrile derivatives were used during the photopolymerization processes under UV light with $\lambda_{\text{max}} = 365$ nm.

3.2. Free-radical photopolymerization under UV light with $\lambda_{\text{max}} = 320$ nm.

Trimethylolpropane triacrylate (TMPTA, from Sigma Aldrich) and 2,2-dimethoxy-2-phenylacetophenone (DMPA, from Sigma Aldrich), were employed as a methacrylate monomer and a free-radical photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, from Sigma Aldrich) for the compositions polymerized by a free-radical mechanism for FPT experiments under UV light with $\lambda_{\text{max}} = 320$ nm.

3.3. Free-radical photopolymerization under UV light with $\lambda_{\text{max}} = 365$ nm.

For the compositions polymerized by a free-radical mechanism under UV light with $\lambda_{\text{max}} = 365$ nm were used trimethylolpropane triacrylate (TMPTA, from Sigma Aldrich) as a model acrylate monomer and the bimolecular systems based on diphenyliodonium hexafluorophosphate (HIP) and 2-amino-4,6-diphenyl-pyridine-3-carbonitrile derivatives as photoinitiators.

3.4. Thiol-ene photopolymerization under UV light with $\lambda_{\text{max}} = 320$ nm.

Moreover, trimethylolpropane trimethacrylate (TMPTMA, from Sigma Aldrich) and trimethylolpropane tris(3-mercaptopropionate) (MERCAPTO, from Sigma Aldrich) were utilized as a methacrylate and thiol monomers for the compositions polymerized by the thiol-ene mechanism. 2,2-dimethoxy-2-phenylacetophenone (DMPA, from Sigma Aldrich) was applied as the photoinitiator in the thiol-ene polymerization process for FPT experiments under UV light with $\lambda_{\text{max}} = 320$ nm.

3.5. Thiol-ene photopolymerization under UV light with $\lambda_{\text{max}} = 365$ nm.

Respectively, trimethylolpropane trimethacrylate (TMPTMA, from Sigma Aldrich) and trimethylolpropane tris(3-mercaptopropionate) (MERCAPTO, from Sigma Aldrich) were applied as the monomers for thiol-ene process of photopolymerization. For the role of UV -long wavelength photoinitiators were used diphenyliodonium hexafluorophosphate (HIP) and 2-amino-4,6-diphenyl-pyridine-3-carbonitrile derivatives. Structures of the monomers are shown in Table 1.
Table 1. Chemical structures of the monomers and iodonium salt.

| Monomers         |
|------------------|
| CADE             |
| TEGDVE           |
| TMPTA            |
| MERCAPTO         |
| TMPTMA           |

4. *References:*

[48] Kambe, S., Saito, K., Sakurai, A., Midorikawa, H., A simple method for the preparation of 2-amino-4-aryl-3-cyanopyridines by condensation of malononitrile with aromatic aldehydes and alkyl ketones in the presence of ammonium acetate, *Synthesis* 1980, 366-368