

Electronic Supporting Information

A Triazolium-Based Fluorophore Intercalated in Layered Double Hydroxides: from Simple Syntheses to Bright Solid-State Luminescence

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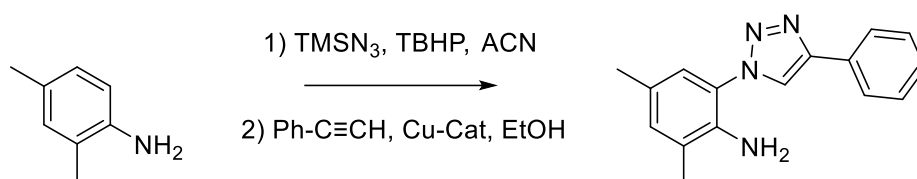
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Details of organic synthesis

General details for organic synthesis: all reactant and solvent were bought from standard suppliers and used as such. For all reactions, no inert atmosphere was used unless mentioned.

Characterization of organic compounds: NMR spectra were recorded with a Bruker AVANCE 400 spectrometer (^1H at 400 MHz, ^{13}C at 100 MHz) at 298 K. Data are reported as chemical shifts (δ) in ppm. Residual solvent signals were used as internal references (^1H , ^{13}C). Electrospray high resolution mass spectra were recorded on a Q-TOF microspectrometer (Waters), using internal (H_3PO_4) and external lock masses (leucine enkephalin $[\text{M}+\text{H}]^+$: $m/z = 556.2766$). IR spectra were collected in the ATR mode with a Perkin Elmer Spectrum Two spectrometer.

Synthesis of precursors of triaz2

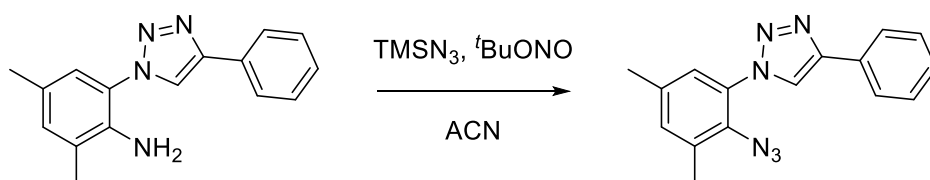


The protocol for azidation reaction was adapted and scaled-up from Tang and Jiao.¹ CuBr (580 mg, 4.04 mmol, 10 mol-%) was added to a round-bottomed flask which was conditioned with a septum under argon. 16 mL of acetonitrile were added and the solution was further degassed for 5 min by argon bubbling. The substrate and the reagents were added through the septum in the following order: 1) 2,4-dimethylaniline (5.00 mL, 4.90 g, 40.44 mmol, 1 equiv.), 2) TMSN₃ (5.9 mL, 5.121 g, 44.45 mmol, 1.1 equiv.) and THBP (7.3 mol.L⁻¹ in water, 6.00 mL, 43.8 mmol, 1.08 equiv.). After 1h, the dark reaction mixture was subjected to TLC analysis (CH₂Cl₂) shows the formation of a major product (R_f = 0.8). The reaction was filtered through a silica pad, which was washed with dichloromethane. After solvent evaporation, a crude black solid (m = 5.06 g) was obtained of the desired azide (^1H -NMR and IR analyses indicate the presence of the desired product as major constituent by comparison with reported data¹. NMR integration allowed us to estimate that the sample contained ~3.9 g (24 mmol) of the desired product, with unreacted starting material as the other major constituent. This material was used as such for the CuAAC reaction. The CuAAC catalyst used was previously reported.² The crude solid obtained in the previous step was dissolved in 40 mL of ethanol (96%) and 80.3 mg (0.12 mmol, 0.5 mol-%) of the [CuCl(SiMe₃)(phenCl₂)] precatalyst were added followed by 3.00 mL of phenylacetylene (2.79 g, 27.32 mmol, 1.14 equiv.). The reaction mixture was stirred at 40 °C for 2 h after which TLC analysis (CH₂Cl₂) showed that all azide was converted and that a product appeared at R_f = 0.4. After this, the solvents and excess phenylacetylene were evaporated (rotary evaporator then high-vacuum pump), and the resulting slurry was treated with 100 mL of a 3:1 diethyl ether : *n*-pentane mixture and placed in a freezer (-30 °C). The product in a crystalline form was recovered by filtration and washed with the same solvent mixture. 5.89 g (22.28 mmol) of brownish crystals were obtained (55% yield over 2 steps).

^1H NMR (400 MHz, CDCl₃): δ 8.03 (s, 1H, CH_{triazole}), 7.91 (m, 2H, CH_{Ph}), 7.46 (m, 2H, CH_{Ph}), 7.37 (tt, 1H, $J_1 = 7.5$ Hz, $J_2 = 1.5$ Hz, CH_{Ph}), 7.01 (bs, 1H, CH_{Ar}), 6.97 (bs, 1H, CH_{Ar}), 4.34 (bs, 2H, NH₂), 2.29 (s, 3H, CH₃), 2.24 (s, 3H, CH₃). ^{13}C NMR (100 MHz, CDCl₃): δ 147.7 (C_q), 137.0 (C_q), 132.2 (CH), 130.4 (C_q), 129.1 (CH), 128.5 (CH), 127.3 (C_q), 126.0 (CH), 124.9 (C_q), 123.0 (C_q), 122.8 (CH), 120.8 (CH), 20.4 (CH₃), 17.9 (CH₃). FT-IR: 3461 (w), 3357(w), 3138(w), 2916 (w), 1673 (m), 1600 (m), 1500 (s), 1233 (m), 1025(m), 763(s), 693(s). ESI-HRMS calcd./found for C₁₆H₁₇N₄ {M+H}⁺: 265.1448/265.1446.

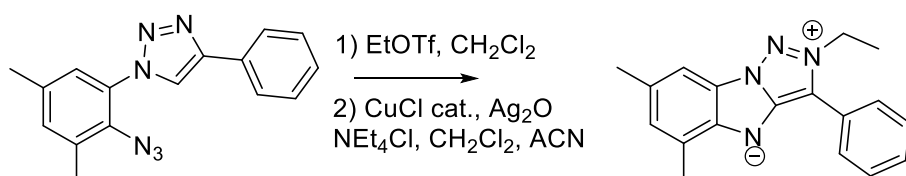
¹ C. Tang and N. Jiao, *J. Am. Chem. Soc.*, 2012, **134**, 18924–18927.

² M. L. Teyssot, L. Nauton, J. L. Canet, F. Cisnetti, A. Chevy and A. Gautier, *Eur. J. Org. Chem.*, 2010, 3507–3515



The starting material (4.58 g, 17.3 mmol) was dissolved in 70 mL acetonitrile. The solution was cooled to 0°C with a ice-water bath. To this solution were added in sequence and with precaution 3.1 mL (2.69 g, 26.1 mmol, 1.5 equiv.) of *tert*-butyl nitrite and 4.1 mL of trimethylsilyl azide (3.59 g, 31.2 mmol, 1.8 equiv.). After 1.5 h, NMR analysis of an aliquot of the reaction mixture indicated full conversion to a single product. The reaction mixture was filtered through a pad of silica which was washed with 40 mL of dichloromethane. After evaporation, 4.69 g (16.2 mmol) of the desired product were obtained (93% yield) as an oil that slowly crystallized.

^1H NMR (400 MHz, CDCl_3): δ 8.13 (s, 1H, $\text{CH}_{\text{triazole}}$), 7.93 (m, 2H, CH_{Ph}), 7.47 (m, 2H, CH_{Ph}), 7.38 (m, 1H, CH_{Ph}), 7.24 (bs, 1H, CH_{Ar}), 7.16 (bs, 1H, CH_{Ar}), 2.43 (s, 3H, CH_3), 2.37 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 136.3 (C_q), 133.6 (C_q), 133.5 (CH), 130.6 (C_q), 130.4 (C_q), 129.3 (C_q), 129.1 (CH), 128.6 (CH), 126.2 (CH), 125.5 (CH), 120.1 (C_q), 20.9 (CH_3), 18.3 (CH_3). FT-IR: 3095(w), 2950(w), 2127(s); 1479 (s), 763(s), 693(s). ESI-HRMS calcd./found for $\text{C}_{16}\text{H}_{17}\text{N}_4$ $\{M+H\}^+$: 291.1353/291.1350.



The starting azido-triazole (2.22 g, 7.64 mmol, 1 equiv.) was dissolved in 40 mL of dichloromethane. 1.75 mL (2.40 g, 13.50 mmol, 1.6 equiv.) of ethyl triflate were added. The reaction was allowed to proceed overnight at room temperature. TLC analysis (CH_2Cl_2) showed a total conversion to a $R_f \approx 0$ product as expected for an intermediate *N*-ethyltriazolium salt. After solvent evaporation, a brown viscous oil was obtained and used for the next step without further purification. ^1H NMR analysis showed a major product bearing the characteristic signals of the ethyl chain.

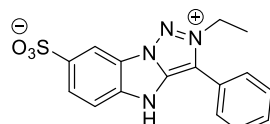
The intermediate triazolium salt was dissolved in 120 mL of a dichloromethane/acetonitrile mixture (v/v 1:1). To the resulting solution were added NEt_4Cl (1.327 g, 8.01 mmol, 1.05 equiv.), Ag_2O (0.969 g, 4.18 mmol, 0.55 equiv.) and CuCl (80 mg, 10 mol-%). The reaction was allowed to proceed with stirring at 50°C for 16h. After this, TLC analysis (acetone + 1% NEt_3) showed full conversion to a single product showing intense blue fluorescence under 365 nm irradiation. The reaction medium was filtered over Celite (washed with ~ 50 mL dichloromethane) to remove inorganic by-products. This organic phase was washed with 2×100 mL aq. NH_3 (1.2 mol/L), 100 mL brine and 100 mL deionized water. After drying over Na_2SO_4 and evaporation, 2.09 g of a crude solid were obtained. This material was triturated in 10 mL of a mixture of diethyl ether and acetone (v/v 3 : 1) to recover 1.66 g (5.72 mmol, 74% yield) of a pure material

^1H NMR (400 MHz, CDCl_3): δ 7.83 (m, 2H, CH_{Ph}), 7.65 (s, CH_{Ar}), 7.58 (m, 2H, CH_{Ph}), 7.48 (m, 1H, CH_{Ph}), 7.24 (bs, 1H, CH_{Ar}), 7.12 (s, 1H, CH_{Ar}), 4.67 (q, 2H, CH_2), 2.71 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 1.68 (t, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 148.0 (C_q), 146.5 (C_q), 129.6 (CH), 129.2 (CH), 129.1 (C_q), 129.0 (CH),

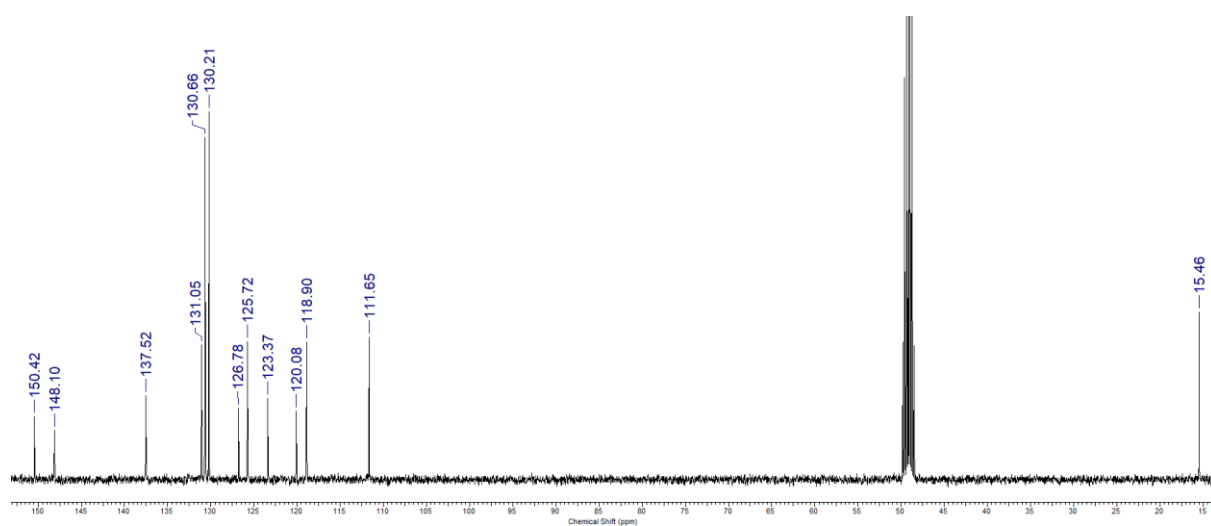
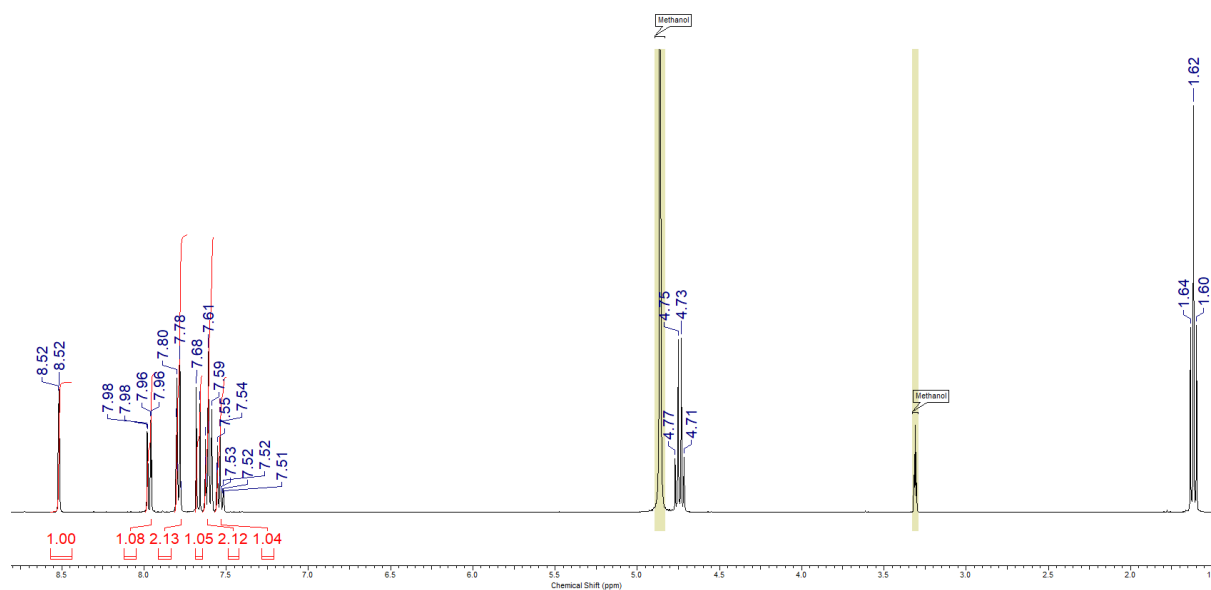
128.1(C_q), 127.7 (CH), 126.7 (C_q), 123.1 (C_q), 118.0 (C_q), 108.9 (CH), 46.7 (CH₂), 21.7 (CH₃), 20.9 (CH₃), 18.3 (CH₃). FT-IR: 2914(w), 1591(m), 1149(m), 1372(m), 1206(s), 1097 (m), 844(s), 774(s), 730(s). ESI-HRMS calcd./found for C₁₈H₁₉N₄ {M+H}⁺: 290.1604/290.1603.

The same procedure (except recrystallization solvent: 96°C EtOH) was applied for the scaffold with R=H. The product was obtained with 81% yields. Analyses of the final product matched previous reports.³

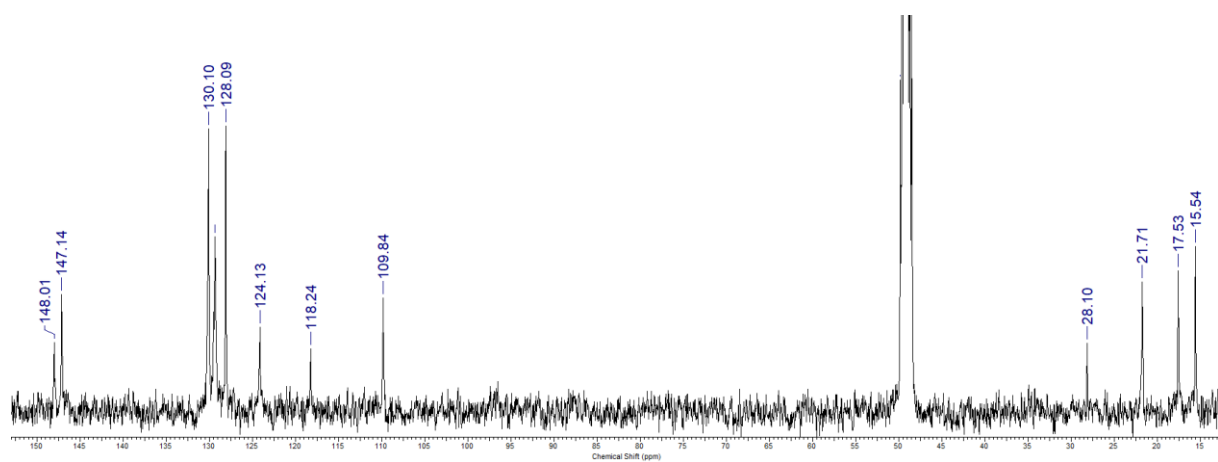
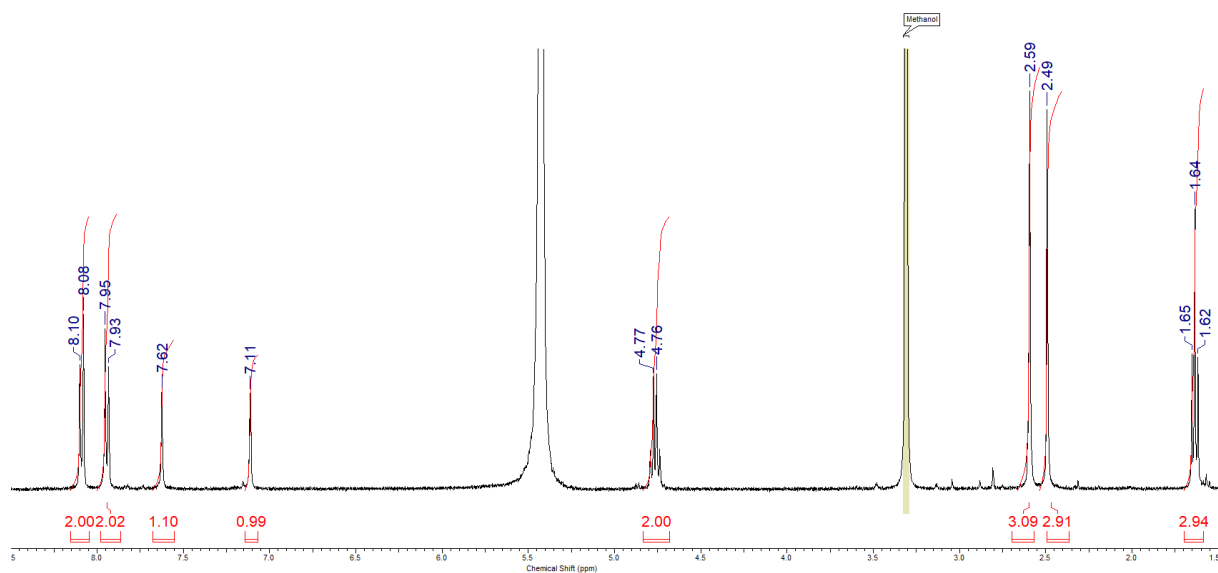
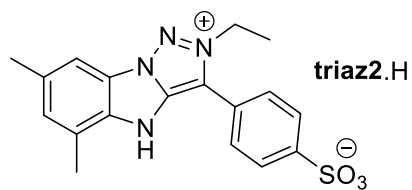
¹H and ¹³C NMR spectra of the sulfonated compounds



triaz1.H



³ K. Bouchemella, K. Fauché, B. Anak, L. Jouffret, M ; Bencharif, F. Cisnetti, *New. J. Chem.* 2018, **42**, 18969-18978



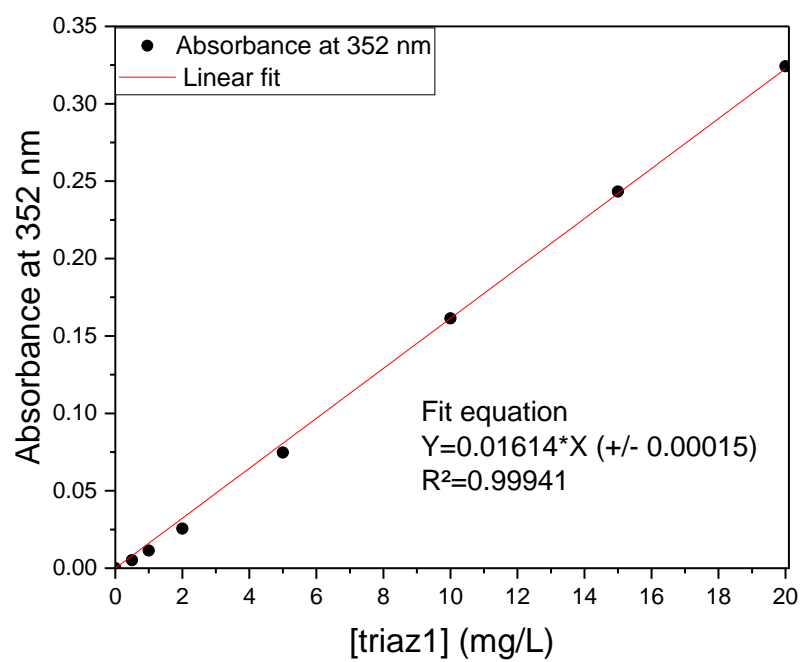


Fig. S1. Absorbance calibration line for the titration of supernatants.

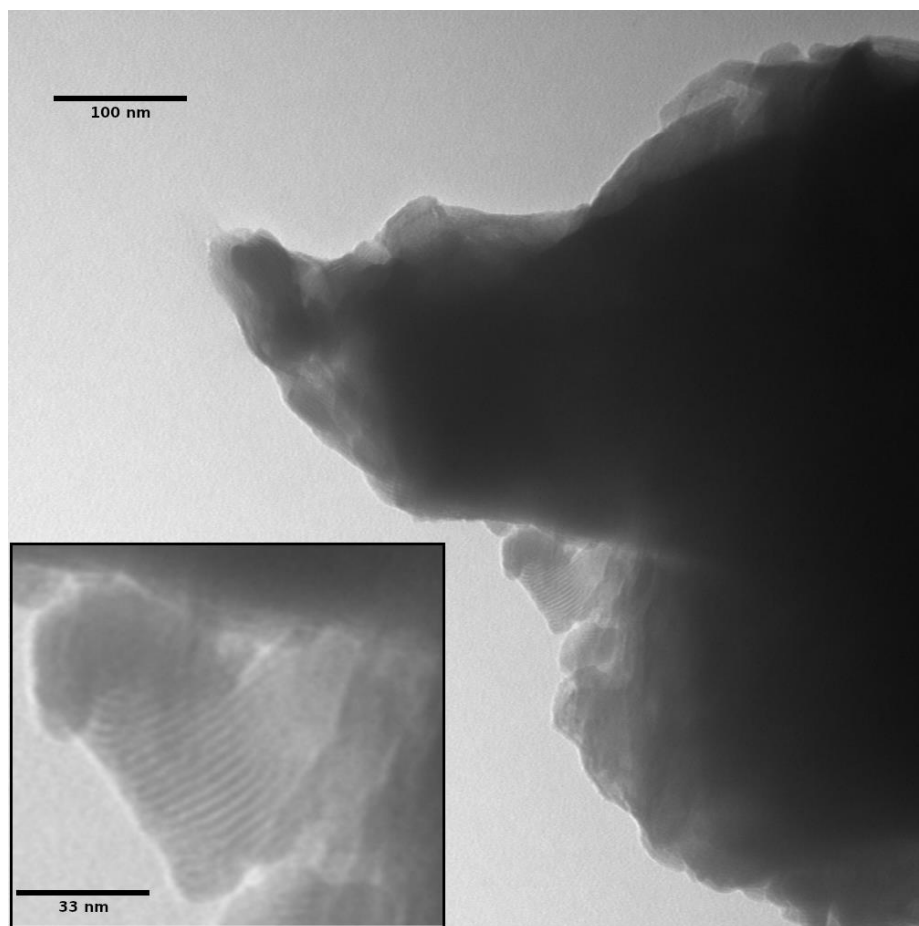


Fig. S2. TEM image of the ZNAL-PPA-triaz1(10%) powder. Inset shows the stacking of layers.

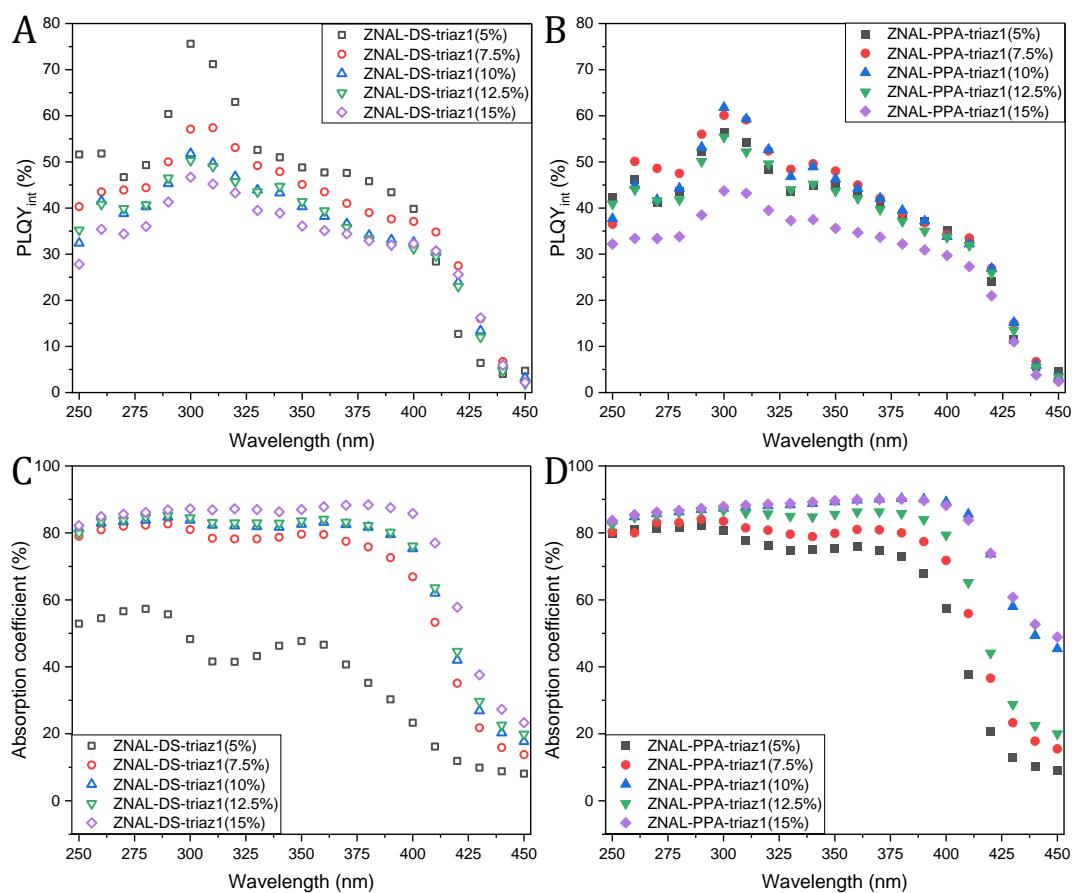


Fig. S3. PLQY_{int} of the (A) ZNAL-DS-triaz1 and (B) ZNAL-PPA-triaz1 powders under excitation wavelengths from 250 to 450 nm. Absorption coefficient of the (C) ZNAL-DS-triaz1 and (D) ZNAL-PPA-triaz1 powders under excitation wavelengths from 250 to 450 nm.

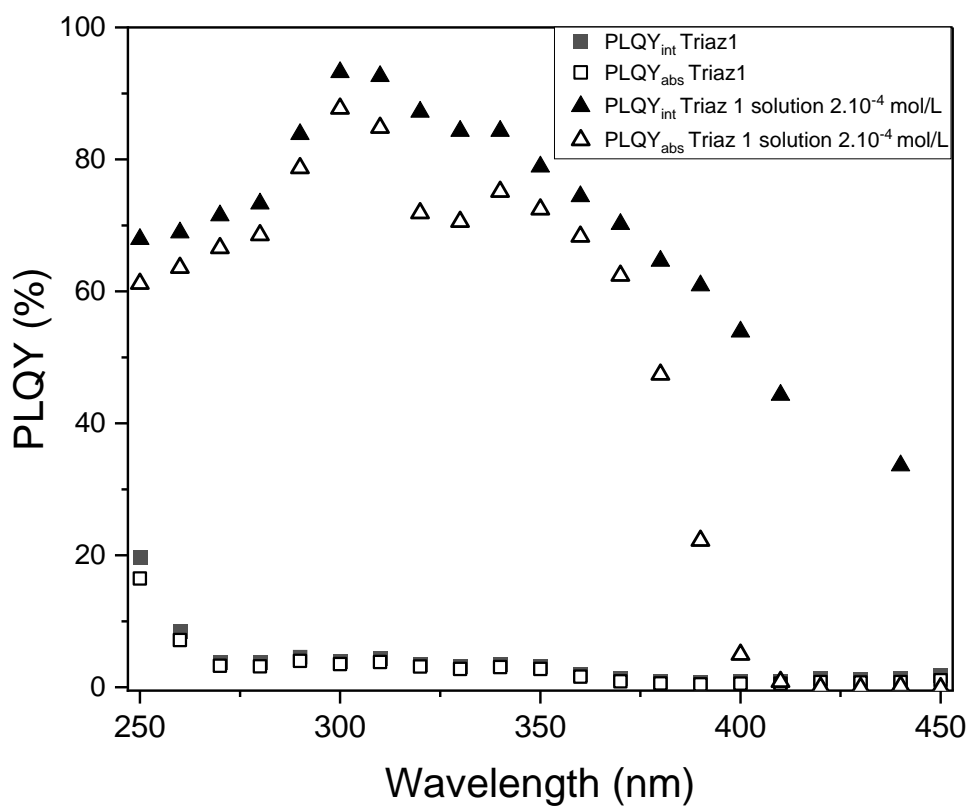


Fig. S4. PLQY_{int} and PLQY_{abs} of the pristine triaz1 fluorophore and of a triaz1 aqueous solution (2.10⁻⁴ mol.L⁻¹).

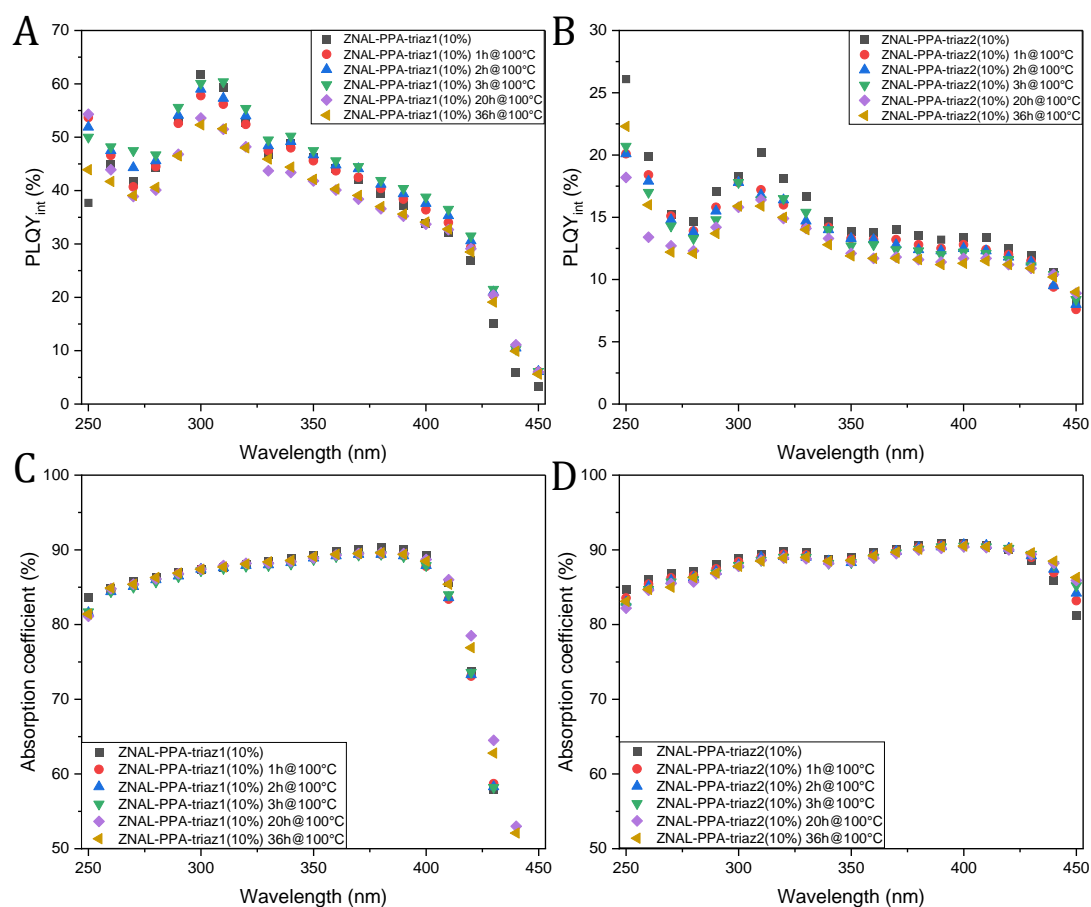


Fig. S5. PLQY_{int} of (A) ZNAL-PPA-triaz1(10%) and (B) ZNAL-PPA-triaz2(10%) powders after a 100°C thermal treatment over several durations. Absorption coefficients of (C) ZNAL-PPA-triaz1(10%) and (D) ZNAL-PPA-triaz2 powders after a 100°C thermal treatment over several durations.

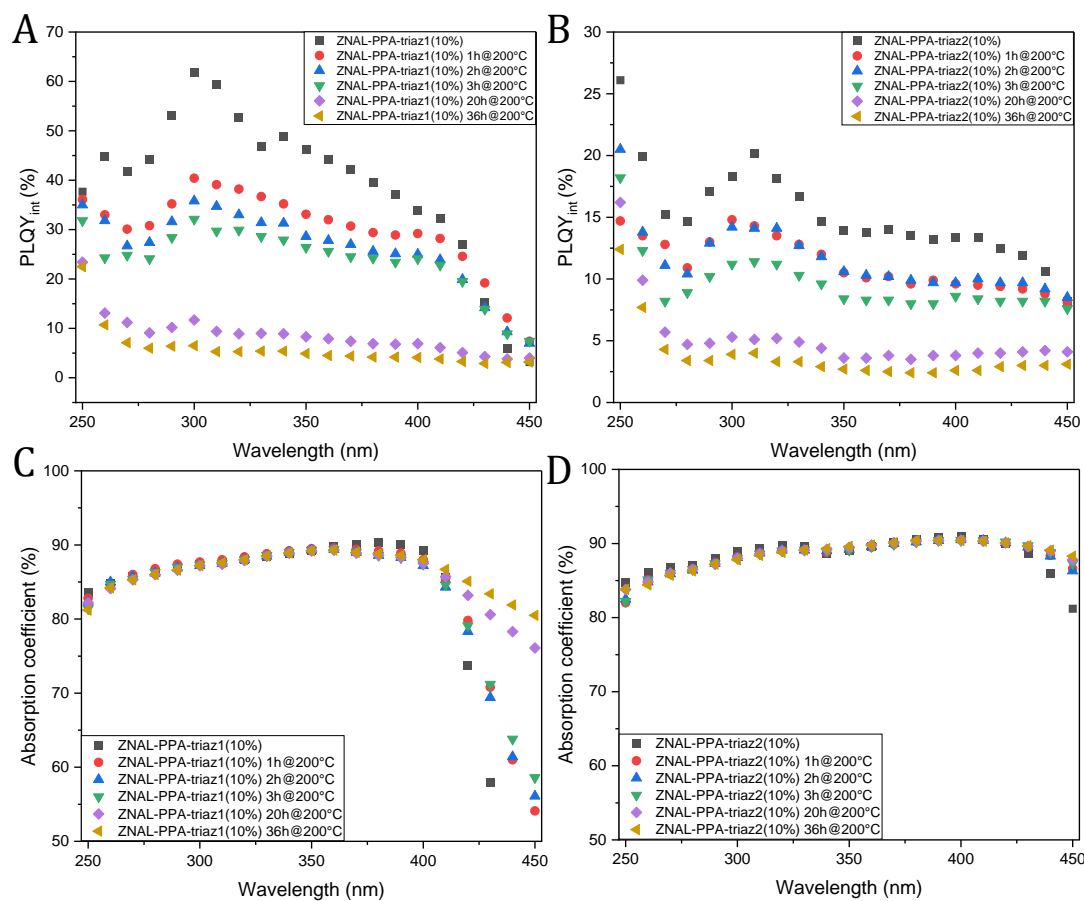


Fig. S6. PLQY_{int} of (A) ZNAL-PPA-triaz1(10%) and (B) ZNAL-PPA-triaz2(10%) powders after a 200°C thermal treatment over several durations. Absorption coefficients of (C) ZNAL-PPA-triaz1(10%) and (D) ZNAL-PPA-triaz2 powders after a 200°C thermal treatment over several durations.

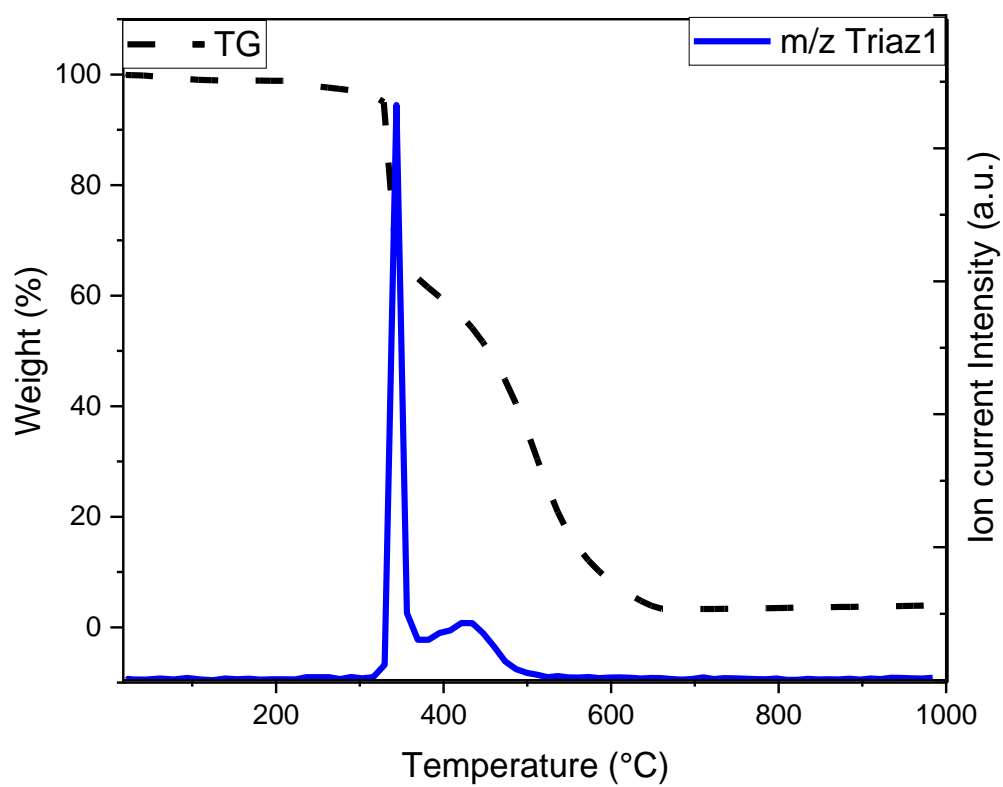


Fig. S7. TGA curve of the ZNAL-PPA-triaz1(10%) powder coupled with mass spectrometry.

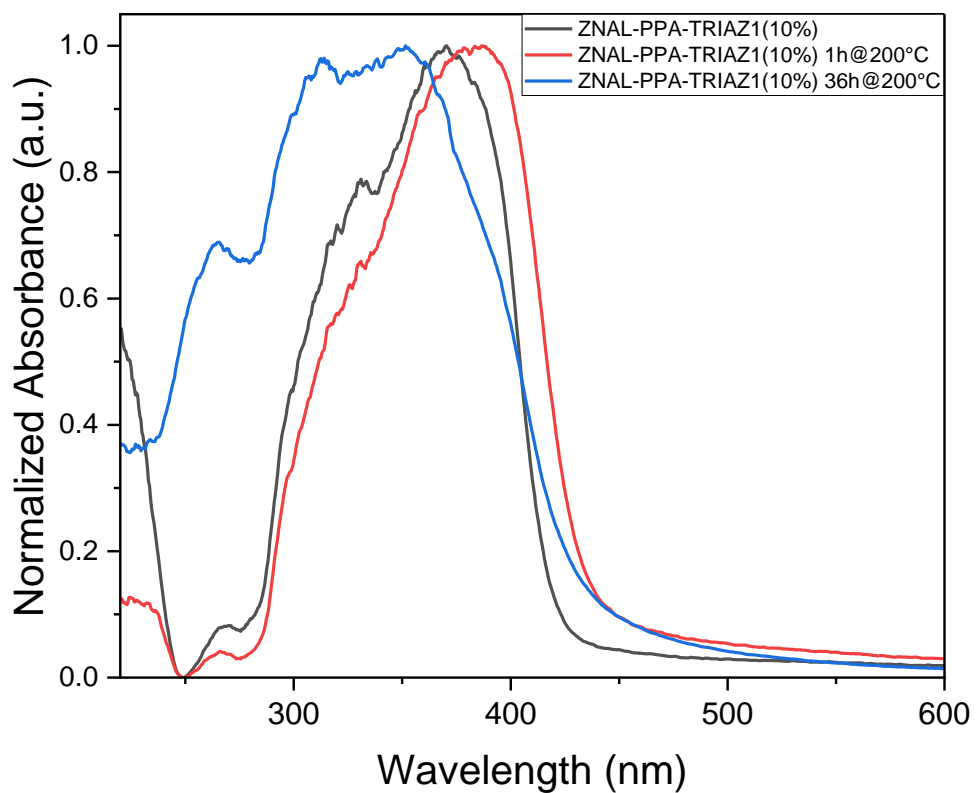


Fig. S8. UV-vis (diffuse reflectance) of the ZNAL-PPA-triaz1 powder (pristine and after 1 h and 36 h of thermal treatment at 200°C).

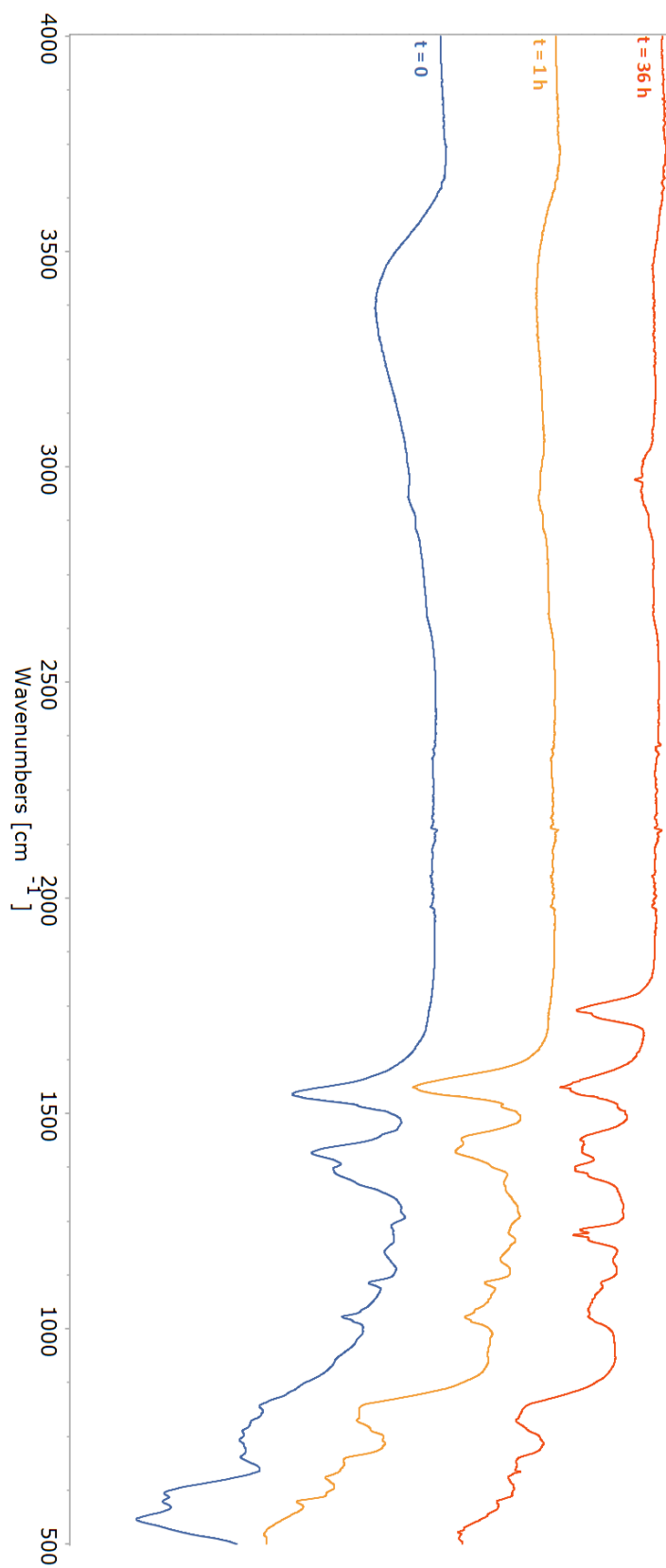


Fig. S9. IR spectra of the ZNAL-PPA-triaz1 powder (pristine and after 1h and 36h of thermal treatment at 200°C).

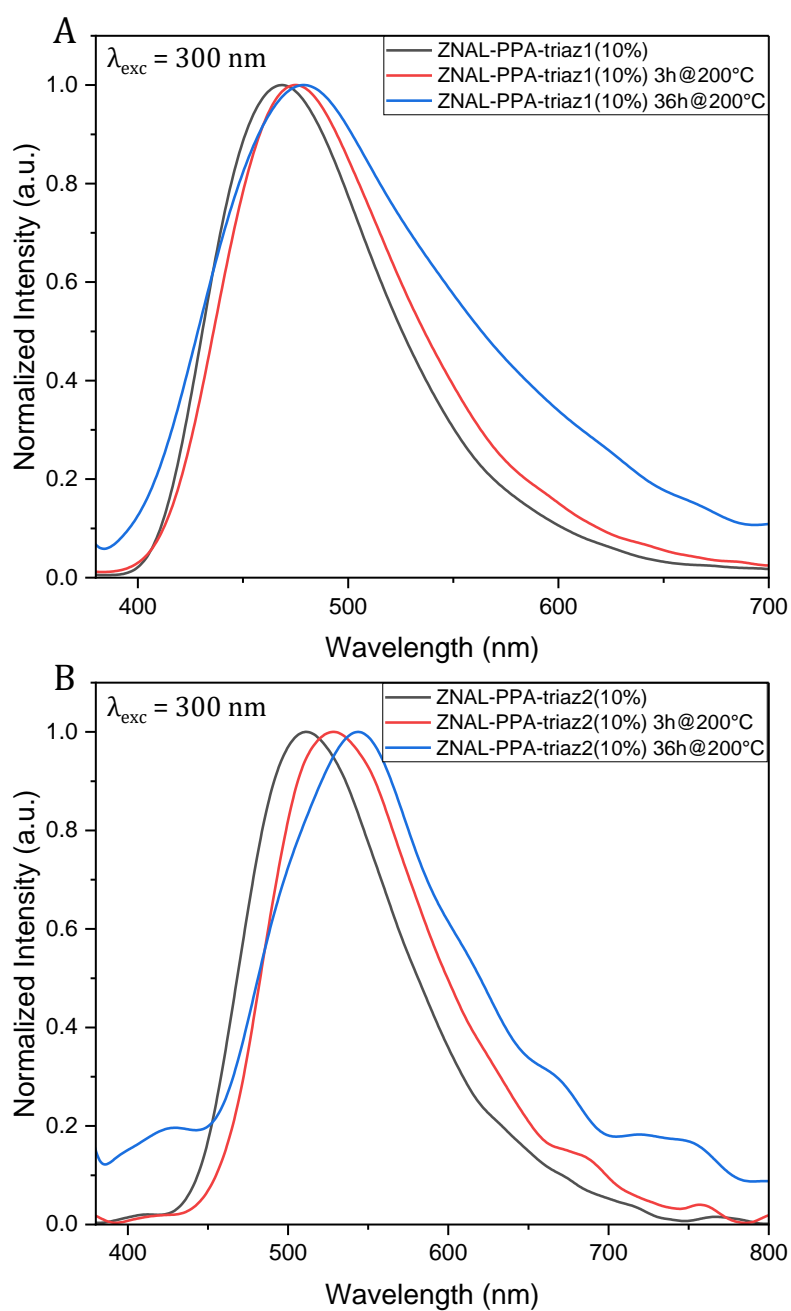


Fig. S10. Emission spectra under 300 nm excitation of (A) ZNAL-PPA-triaz1(10%) and (B) ZNAL-PPA-triaz2(10%) powders over thermal treatment at 200°C.

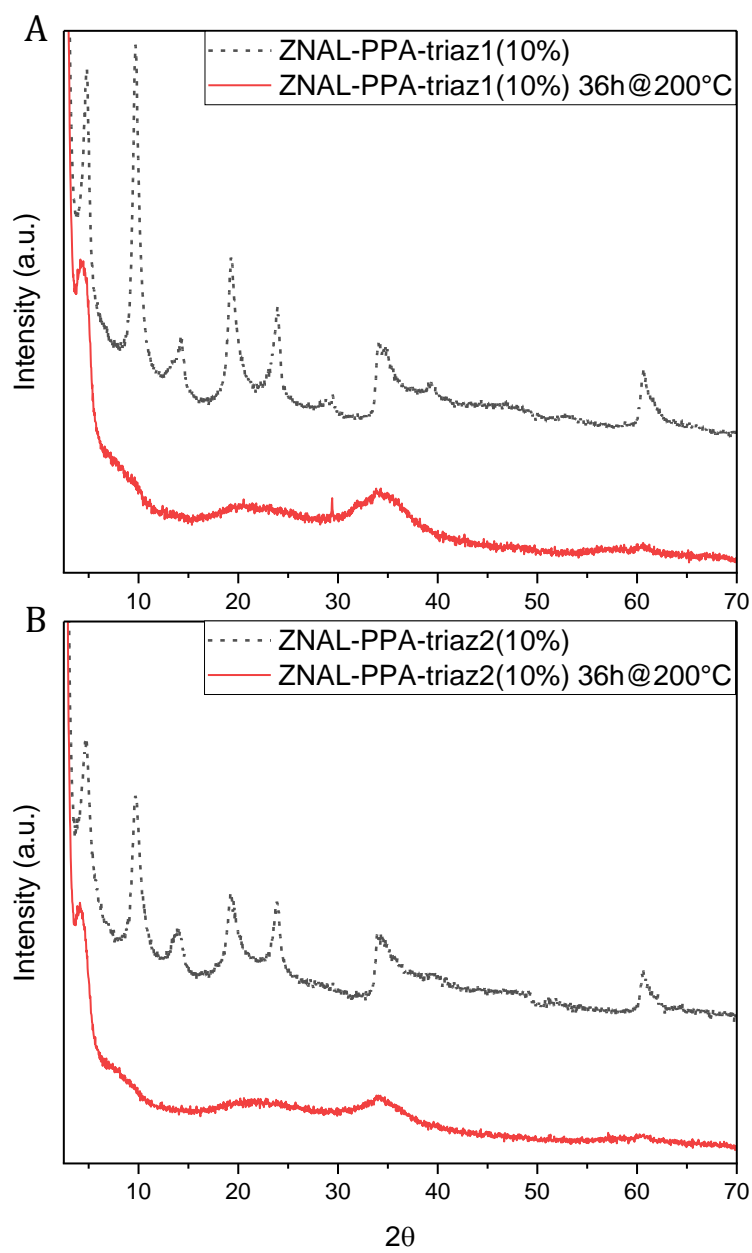


Fig. S11. XRD patterns of (A) ZNAL-PPA-triaz1(10%) and (B) ZNAL-PPA-triaz2(10%) powders before and after 36h at 200°C.