Electronic Supporting Information

Synthesis and characterization of a new triazine-based NUV-Blue excitable material for phosphor-converted LED technologies

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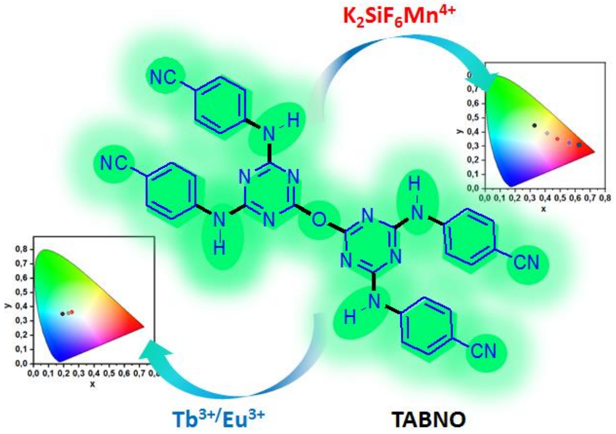

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1. Materials and methods.

All chemicals were purchased from TCI chemicals or Aldrich and used without further purification. ^{1}H NMR spectra were recorded on a 500 MHz Varian spectrometers at 27°C using deuterated DMSO (ref. 2.50 ppm) as a solvent Chemical shifts (δ) are given in ppm. Coupling constants (J) are reported in Hz. Fourier transform infrared spectroscopy measurements were carried out on a Bruker Tensor 27 spectrophotometer equipped with a diamond-ATR accessory and a DTGS detector. A number of 128 scans with a resolution of 2 cm^{-1} were averaged in the spectral range 4000 cm^{-1} – 400 cm^{-1}. Elemental analysis (Perkin Elmer Series II 2400). Thermogravimetric analysis (TGA) measurements were carried out at atmospheric pressure using a Perkin Elmer instrument model TGA7. The measurements were performed under Ar flow (60 ml min−1). 5 mg of sample were placed in platinum crucible and scanned in the temperature range of 40-800 °C with a heating rate of 10 °C min−1. TGA7 instrument was calibrated with Curie points of Alumel, Nickel, Perkalloy and Iron standard samples and the temperature was obtained with an accuracy of ± 2° C.

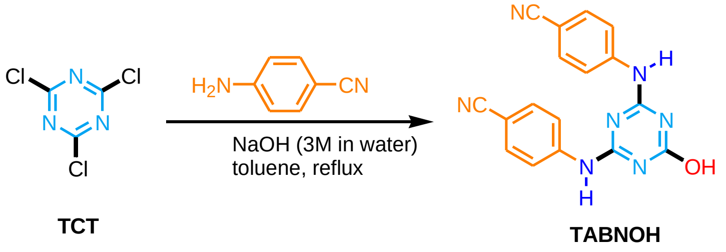
A PerkinElmer instrument (model DSC7) was used to perform the DSC measurements, at atmospheric pressure and under an argon flow of 60 mL min−1. A total of 5 mg of each sample was placed in an aluminium crucible, and measurements were performed in isothermal mode at 270 °C . The instrument was calibrated by measuring the melting temperature of metallic In and Zn (temperature accuracy of ±0.5° C). X-ray powder diffraction (XRPD) patterns were recorded with a Seifert X3000 diffractometer (Ahrensburg, Germany) operating at 30 mA and 40 kV using Cu Kα radiation and equipped with a graphite monochromator on the diffracted beam. Patterns were recorded in a step scan mode in the range $5° \leq 2\theta \leq 80°$ with a step size of 0.05 2θ degree, collecting at least 1000 counts for each step. Samples were deposited on the silicon zero background sample holder.

Time resolved photoluminescence (TR-PL) measurements were recorded by exciting the samples with 200 fs long pulses delivered by an optical parametric amplifier (Light Conversion TOPAS-C) pumped by a regenerative Ti:sapphire amplifier (Coherent Libra-HE). The repetition frequency was 1 kHz and the PL signal was recovered by a streak camera (Hamamatsu C10910) equipped with a grating spectrometer (Princeton Instruments Acton SpectraPro SP-2300). All the measurements were collected in the front face configuration to reduce inner filter effects. Proper emission filters were applied to remove the reflected contribution of the excitation light.

Steady time photoluminescence measurements were performed using the filtered light from a laser driven Xenon lamp (EQ-99X) with a final bandwidth of about 1 nm. The emitted photoluminescence was collected by means of an optical fiber connected to an Avantes Thermo-Electric Cooled spectrometer.

Photoluminescence excitation spectroscopy (PLE) measurements were performed using a Horiba Jobin Yvon FluoroMax-3 spectrofluorometer; three-dimensional mapping was obtained with a 450 W xenon lamp as the excitation source. Three-dimensional maps were collected with an excitation range of 200–600 nm and an emission range of 200–600 nm with a 5 nm slit for excitation and emission.

2. Synthesis and chemical characterization of TABNOH



Cyanuric chloride (184 mg, 1 mmol) was dissolved in toluene (4.0 mL) and 4-aminobenzonitrile (248 mg, 2.1 mmol) was added, followed by 1.0 mL of $NaOH_{acq.}$ (3.0 M). The reaction mixture was refluxed overnight and the resulted suspension was filtered on a glass sinter and washed with water to give TABNOH (4,4'-((6-hydroxy-1,3,5-triazine-2,4-diyl)bis(azanediyl))dibenzonitrile). in 79% yield as a white solid. Mp = 260° C; ^{1}H NMR (400 MHz, DMSO-d_6), δ: 10.04 (s 2H) 8.04 (d, 4H J = 8,63 Hz); 7.79 (d, 4H J = 8,63 Hz). Selected FT-IR ATR data (cm^{-1}): 3128 (br), 1709 (s), 1576 (s), 1508 (s), 1433 (s), 1376 (s), 1254 (s), 1027 (s), 904 (s), 762 (s), 658 (s), 609 (s), 505 (s); HRMS (ESI), calculated for $[M]^+$ $C_{17}H_{11}N_7O$: 329,1025; found: 329,1048.

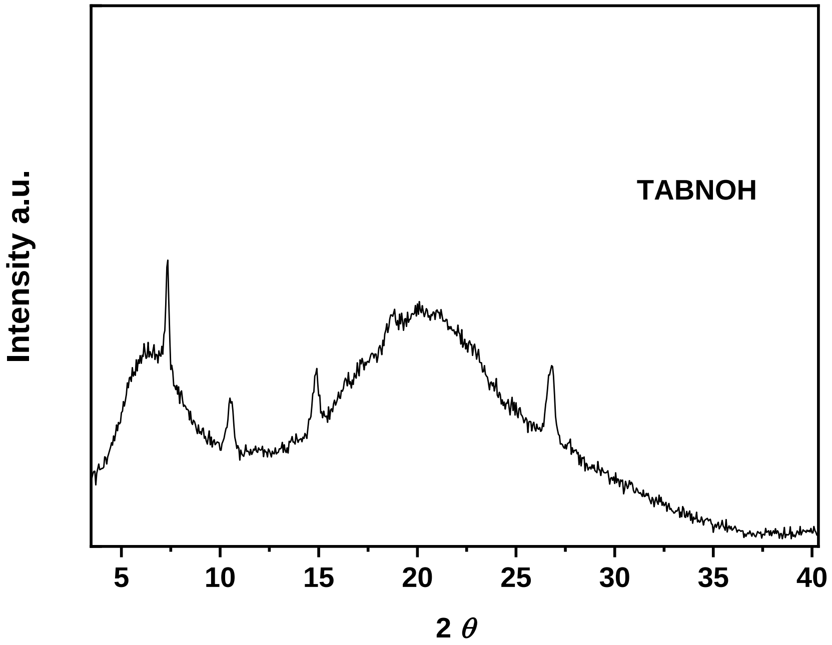
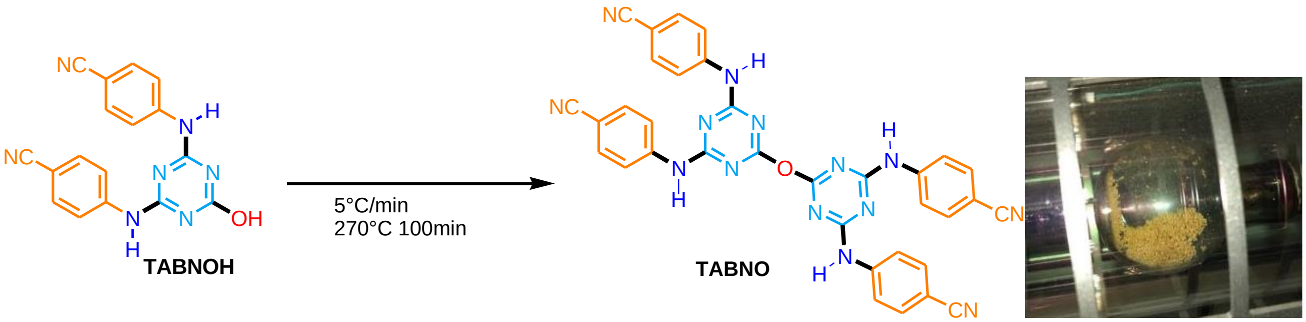
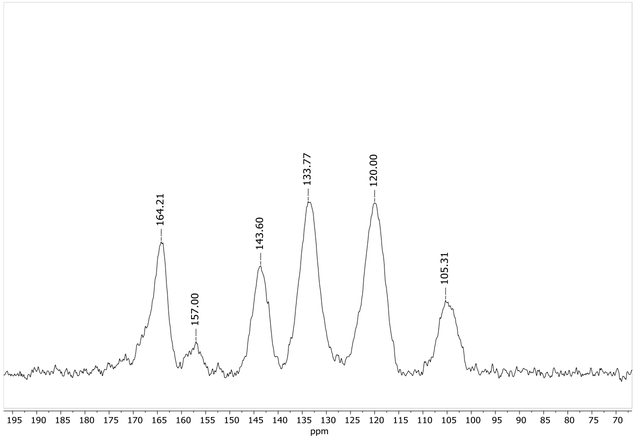


Figure S1. PXRD analysis of TABNOH

3. Synthesis and characterization of TABNO



250 mg (0.76 mmol) of TABNOH were loaded on a Pyrex glass ampule and warmed up to 270°C for 100 minutes by using a Buchi Glass Oven B-585 (5° C/min). The resulting crystalline yellow powder was washed with acetone and dried at 90° for 2 h affording TABNO in 218 mg and 90% of yield. HRMS (MALDI) calculated for $[M]^+$ $C_{34}H_{20}N_{14}O$: 640,202. found: 640,489 (No Matrix); FT-IR (cm^{-1}) ν: 3311, 2221, 1685, 1577, 1486, 1469, 1353, 1240, 1172, 836, 808.



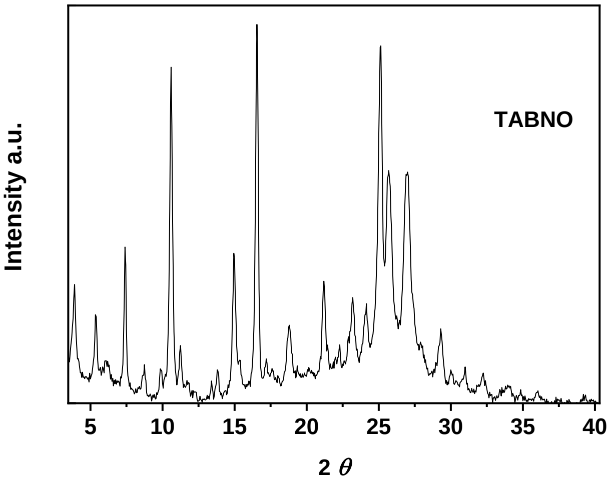


Figure S2. Solid state ^{13}C CP-MAS NMR spectra of TABNO

Figure S3. PXRD of TABNO

4. Characterization and data comparison of TABNO

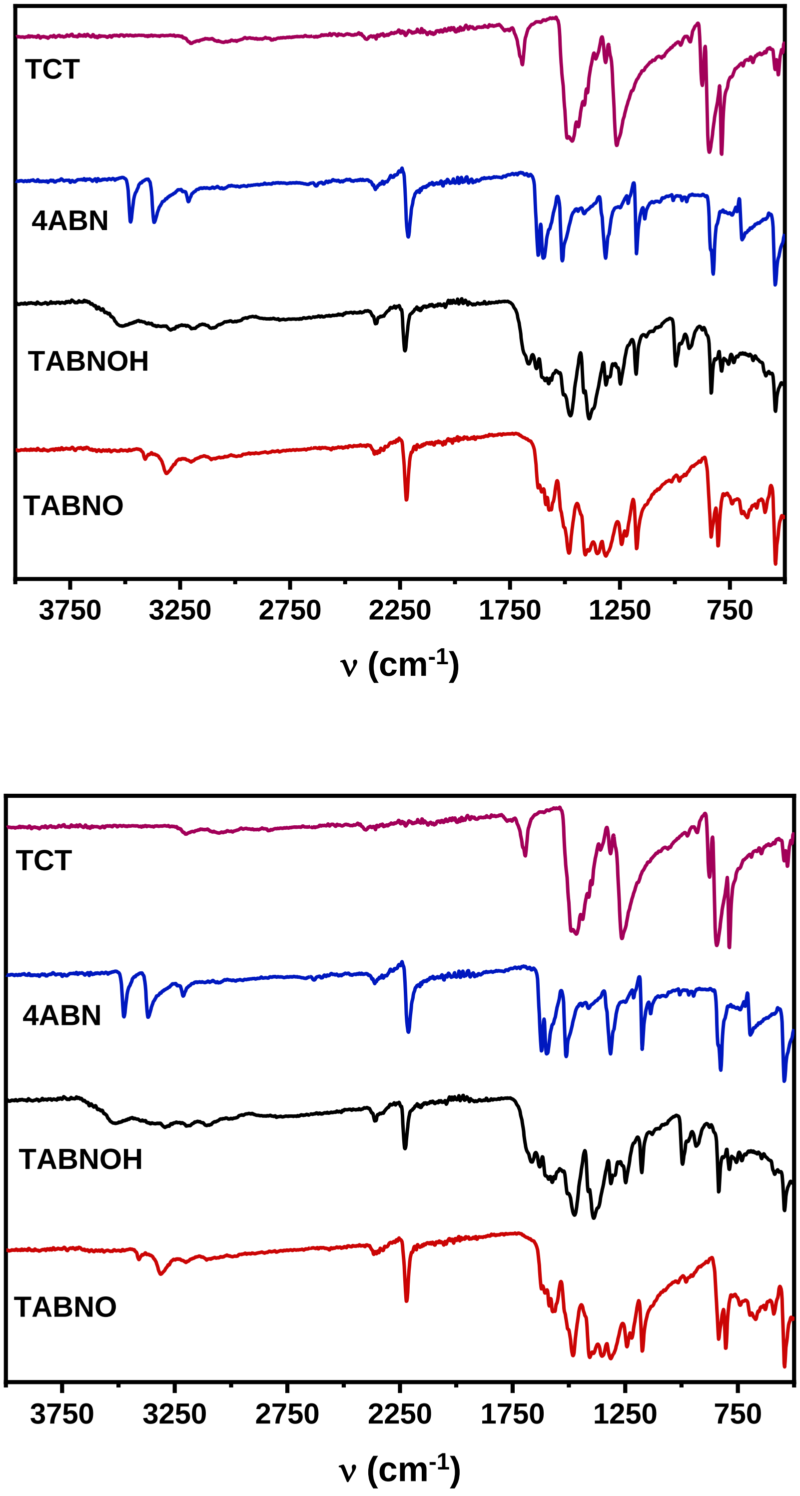


Figure S4. FTIR spectra of cyanuric chloride (purple) 4-amminobenzonitrile (blue) TABNOH (black) TABNO (red).

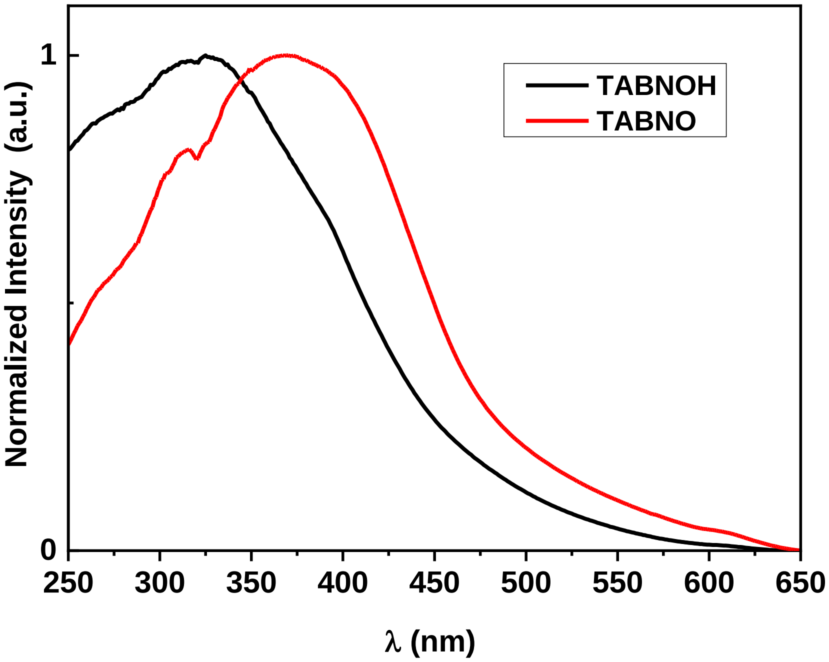


Figure S5. UV-Vis absorption and PL of TABNOH (black) and TABNO (red).

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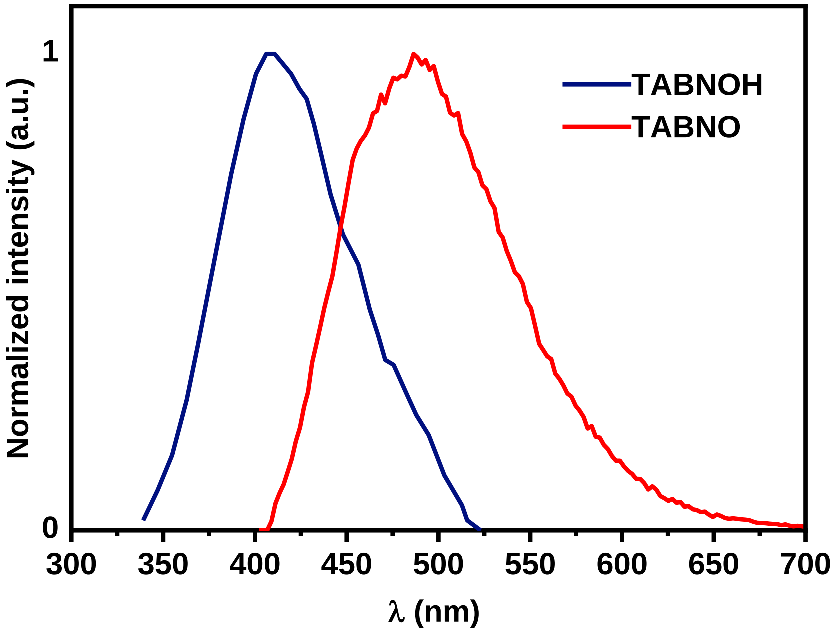

Figure S6. Emission spectra of TABNOH (black) TABNO (red).

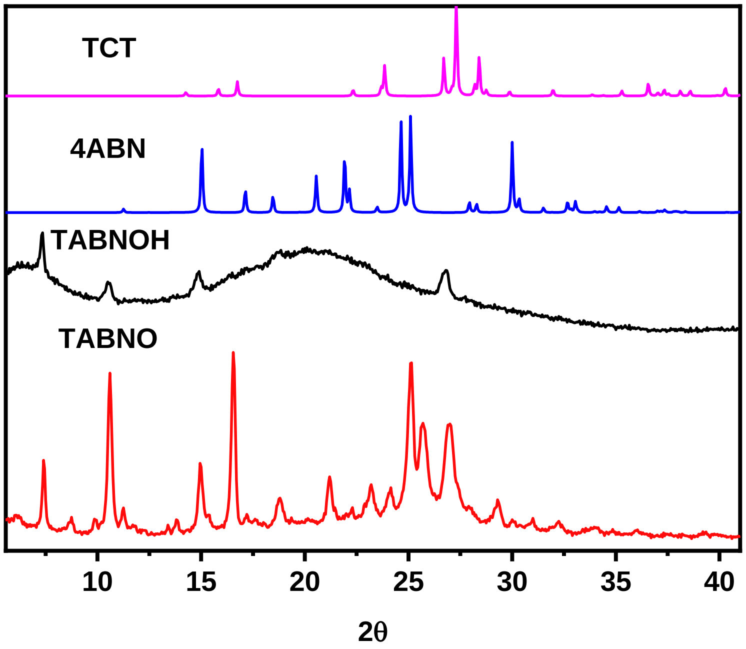

Figure S7. PXRD of cyanuric chloride (pink) 4-amminobenzonitrile (blue), TABNO (red), TABNOH (black).

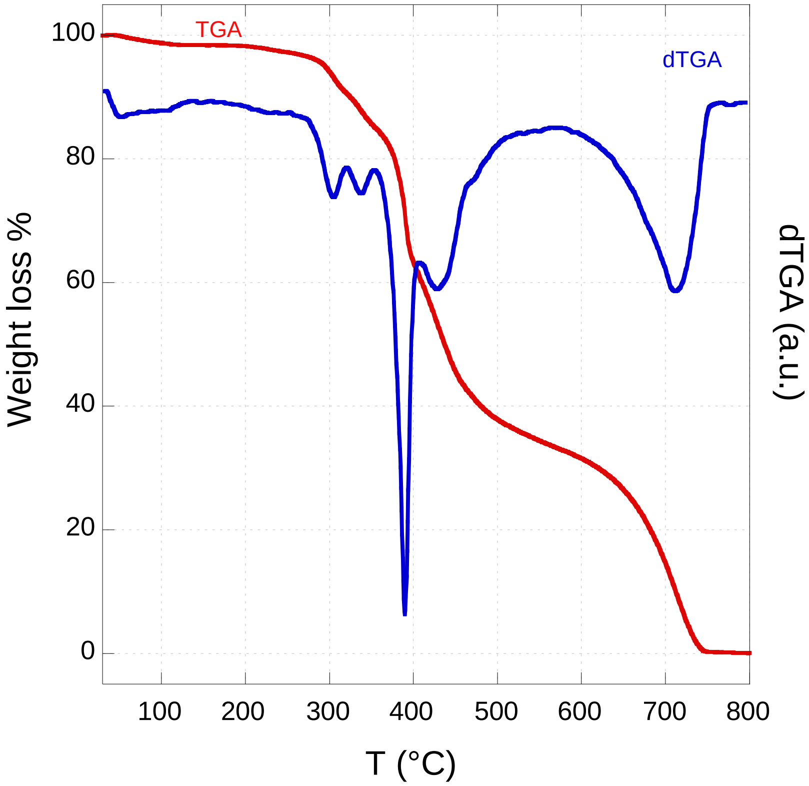

Figure S8. Thermogravimetric analysis of the TABNOH sample, carried out with a heating rate of 10°C/min, shows a step around 273°C. At higher temperature complete decomposition of the sample was observed.

5. References and Notes

1) E. Kroke, M. Schwarz, E. Horath-Bordon, P. Kroll, B. Noll, A. D. Norman, *New J. Chem.*, 2002, **26**, 508–512 (2002).
2) A. M. Islor, B. Chandrakantha, T. Gerber, E. Hosten, R. Betz, *Z. Kristallogr*. 2013, **228**, 217-218
3) K. Xu, D. M. Ho, R. A. Pascal Jr, *J. Am. Chem. Soc*., 1994, **116**, 105-110.