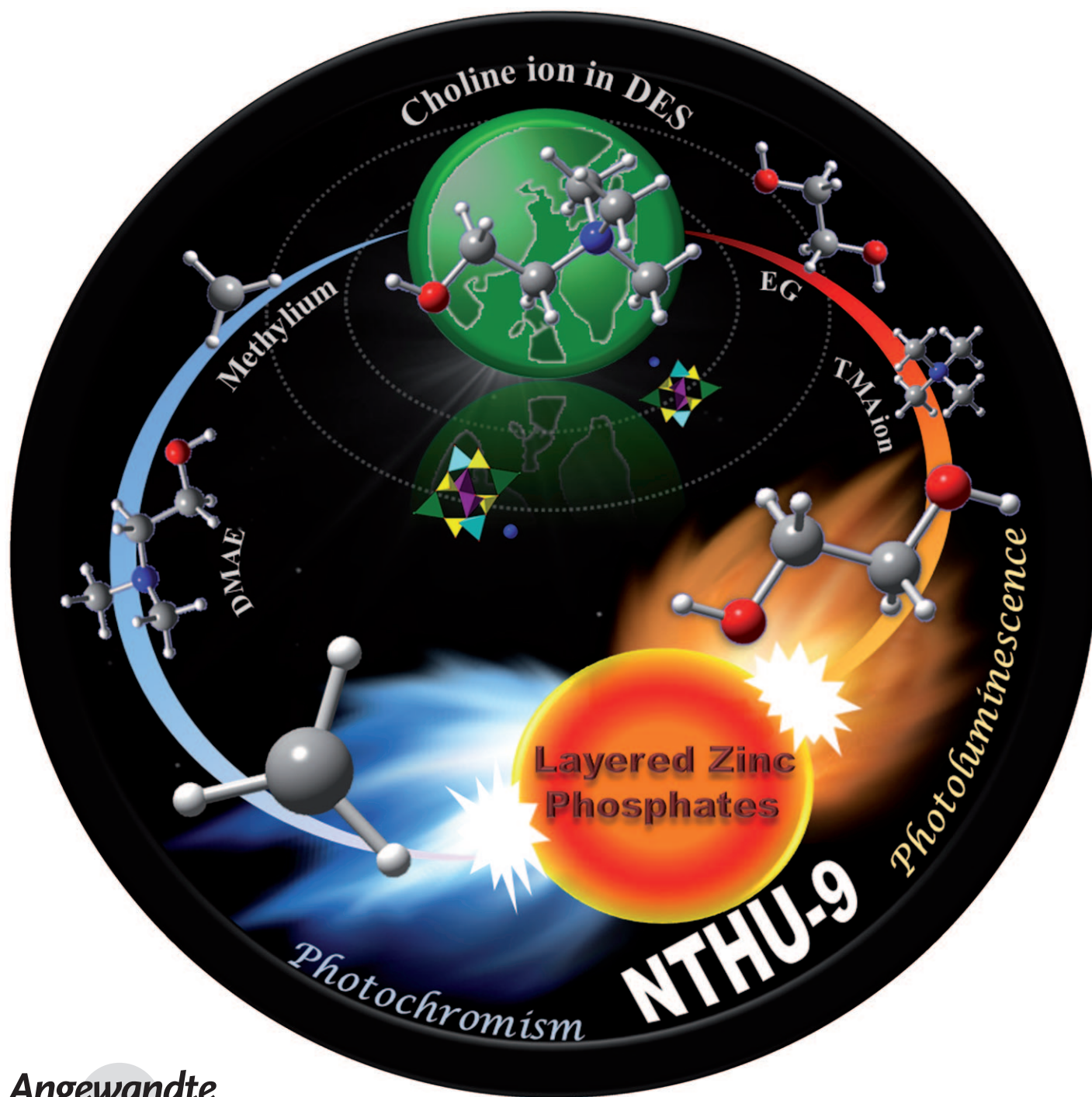


Layered Zinc Phosphates with Photoluminescence and Photochromism: Chemistry in Deep Eutectic Solvents**

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In the synthesis of new functional materials, it is advantageous to seek reaction routes that maximize efficient use of the source chemicals and avoid using toxic and volatile organic solvents. In these regards, choline-based deep-eutectic solvents (DESs)^[1–4] are undoubtedly the ideal, given their biodegradability and versatility in ionothermal reactions.^[5–7] As a type of ionic liquid, DESs are composed of two organic solids: an ionic salt (choline chloride) and a molecular compound (urea/urea derivative or carboxylic acid).^[2] Recently, major advances in creating new functional materials in such choline-based DES systems have been made.^[3,4] Notable examples include a nanotubular structure with activator-free yellow-green photoluminescence (PL) and distinctive MOF materials with hydrogen storage properties.^[3,4] Without exception they all contain ligand, template, or other species derived from DES components. Under ionothermal conditions, the versatility of DES is enhanced by decomposition of its molecular component (urea or urea derivative), which can provide in situ generated building units to increase the structural diversity of the products.^[1] In contrast, the possibility of degradation of the ionic portion of DES was seldom envisaged. To date, chemical reactivity related to the choline ion $[(\text{CH}_3)_3\text{NC}_2\text{H}_5\text{OH}]^+$ in choline-based DESs was not reported.

To prepare new phosphor materials in the system of open-framework metal phosphates (MPOs),^[4,8] we use the DES choline chloride/oxalic acid dihydrate as a benign solvent. Following the yellow-green phosphor NTHU-7,^[4] we have synthesized the first metal-activator-free orange phosphor NTHU-9, which has a unique layered structure of zinc chlorophosphate with occluded organic templates (Figure 1). The DESs formed by carboxylic acid/choline chloride eutectic mixtures are regarded as more stable than those formed by urea and choline chloride and did not contribute decomposition products as templates to the reactions.^[4,9] Intriguingly, by careful scrutiny in both reaction products and filtrates, we identified unexpected fragments which led us to discover two concurrent pathways of chemical reactions involving choline ions under ionothermal conditions (Scheme 1): 1) demethylation of choline ions to give methylum (CH_3^+) ions and 2-(dimethylamino)ethanol (DMAE); 2) hydrolysis of choline ion to ethylene glycol (EG) and trimethylamine, which further reacts with CH_3^+ to give the tetramethylammonium (TMA) ions. The CH_3^+ ions generated in situ in reaction 1 also react with the amine reagents 4,4'-trimethylenedipyridine (tmdp) and 4,4'-bipyridine (bpy) to create N,N' -dimethylated templates, that is, $[(\text{CH}_3)_2\text{tmdp}]^{2+}$ and $[(\text{CH}_3)_2\text{bpy}]^{2+}$. Herein, we report the remarkable orange-

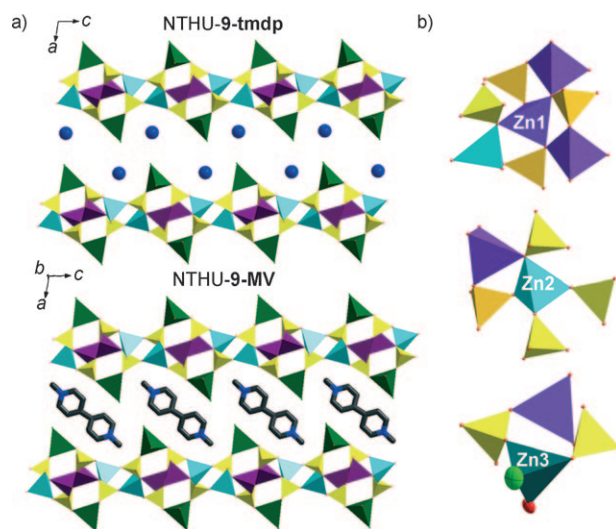
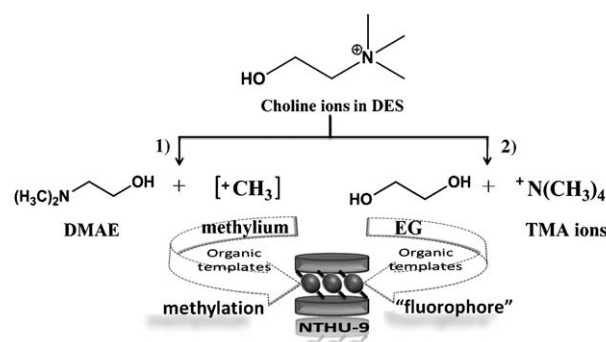


Figure 1. Polyhedral plots of the inorganic layers in NTHU-9. a) Layers with disordered sites for choline ions (only N atom found) in 9-tmdp (top) and dimethylated bpy molecules in 9-MV (bottom). b) Three types of tetrahedral Zn centers with different connectivity. Blue, green, and red balls represent N, Cl, and water O atoms, respectively.



Scheme 1. Two concurrent reactions pathways in choline-based DES under ionothermal conditions. 1) Demethylation of choline ions and subsequent N,N' -methylation of the amine template. 2) Hydrolysis of choline ions to form EG, which entered into NTHU-9 to form "fluorophores" with the amine template.

emitting NTHU-9, which is also the first metal phosphate exhibiting dual properties of photoluminescence and photochromism. Its discovery not only brought us a step forward in the preparation of new phosphors in the MPO system but also unveiled new insights into chemistry and unexplored nature of common choline-based DESs.

Layered zinc phosphate NTHU-9, prepared in choline chloride/oxalic acid dihydrate (1/1), adopts a unique 2D structure (Figure 1). The inorganic $[\text{Zn}_3\text{Cl}(\text{H}_2\text{O})(\text{PO}_4)_2]^-$ layer exhibits an unusually high ratio of Zn/P, presumably due to the higher solubility of ZnO in DESs than in common molecular solvents.^[2c] According to a literature survey,^[10] the ratios of Zn/P for negatively charged ZnPO frameworks are primarily distributed in the range $(n-1)/n$, 1, to $(n+1)/n$, where $n = 2-6$. For each individual ratio there are one or more existent compound(s), except for the highest ratio of $\text{Zn}/\text{P} = 3/2$, which is now represented by NTHU-9.^[11] The $[\text{Zn}_3\text{Cl}-$

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$(\text{H}_2\text{O})(\text{PO}_4)_2]^-$ layer contains three unique tetrahedral Zn^{2+} centers: $\text{Zn}(1)\text{O}_4$ is seven-connected and linked with PO_4 tetrahedra into infinite three-membered-ring (3R) chains via Zn-O-Zn linkages, the only type observed in high Zn/P structures;^[12] $\text{Zn}(2)\text{O}_4$ is five-connected and forms ladderlike 4R chains with PO_4 ; $\text{Zn}(3)\text{O}_2\text{Cl}(\text{H}_2\text{O})$ is an unusual two-connected pendent tetrahedron with the Cl vertex pointing toward the interlayer space. The space between inorganic layers is occupied by choline ions (original DES component), EG molecules (generated in situ from choline, vide infra), and $[(\text{CH}_3)_2\text{tmdp}]^{2+}$ or $[(\text{CH}_3)_2\text{bpy}]^{2+}$ cations (amine reagent methylated in situ), which led to two compounds with different interlayer compositions (Table 1): NTHU-9-tmdp and NTHU-9-MV (abbreviated as 9-tmdp and 9-MV hereafter).

Table 1: Chemical compositions of the counter-species in NTHU-9

Compound ^[a]	A ^[b]	B ^[b]	C ^[b,c]	E ^[b]
9-tmdp	0.70	0.15	–	0.15
9-MV	0.20	–	0.40	0.40

[a] The inorganic framework determined from single-crystal structure analysis was $[\text{Zn}_3(\text{PO}_4)_2\text{Cl}(\text{H}_2\text{O})]^-$. [b] Occluded organic species were identified by NMR and EIMS; relative quantities were determined from TGA and EA data: A: choline ions, B: $[(\text{CH}_3)_2\text{tmdp}]^{2+}$ ions, C: $[(\text{CH}_3)_2\text{bpy}]^{2+}$ ions, and D: ethylene glycol. [c] A certain fraction of $[(\text{CH}_3)_2\text{bpy}]^{2+}$ ions were found to be perhydrogenated to $[(\text{CH}_3)_4\text{bpz}]^{2+}$ ions (Figure S7, Supporting Information); bpz = 4,4'-bipiperazine.

In the structure of 9-tmdp,^[13] all interlayer species are disordered and hardly located in electron-density maps. Their individual presence was confirmed by elemental analysis, thermogravimetric analysis, and ^{13}C solid-state NMR and other spectroscopic measurements. During the course of synthesis, we noticed an unusual ammoniacal odor on opening the digestion bombs. We suspected DMAE, which was later confirmed and detected in reaction filtrates as well. The presence of DMAE in the reaction filtrate signified that choline ions of the DES were demethylated. Furthermore, in electron-impact mass spectra (EIMS) of 9-tmdp, we found unexpected mass fragments corresponding to methylated tmdp. We then assumed tmdp, rather than being protonated as usual, was dimethylated by CH_3^+ generated in situ to form $[(\text{CH}_3)_2\text{tmdp}]^{2+}$ cations, which appeared as a minor counter-species in 9-tmdp. To verify this reaction mechanism, we replaced tmdp with bpy and obtained 9-MV,^[14] which is isostructural with 9-tmdp, and allowed direct identification of dimethylated bpy molecules (Figure 1) in electron-density maps. In stark contrast to the minor part played by $[(\text{CH}_3)_2\text{tmdp}]^{2+}$ in 9-tmdp, $[(\text{CH}_3)_2\text{bpy}]^{2+}$ ions are a major fraction of the counterions in 9-MV. Thus, pathway (1) of Scheme 1 involving choline ion demethylation to DMAE and subsequent *N,N'*-dimethylation of amine reagents was confirmed.

In situ powder X-ray diffraction measurements showed the NTHU-9 structure is retained up to 270 °C for 9-tmdp and 350 °C for 9-MV (Figure S4, Supporting Information). However, unexpected weight losses were observed to start far below these temperatures (Figure S5, Supporting Informa-

tion). They were assumed to correspond to removal of EG molecules, which were identified in the structure of 9-MV by ^{13}C solid-state NMR measurements (see Supporting Information, Figure S7). Ethylene glycol was further found in the reaction filtrates for both 9-tmdp and 9-MV. The amounts of EG in the individual compounds was determined from the early weight losses in their TG curves: about 1.5 % for 9-tmdp up to 250 °C and about 4.3 % for 9-MV up to 330 °C, which yielded 0.15 EG per formula unit of 9-tmdp and 0.4 EG per formula unit of 9-MV. Successive weight losses at higher temperatures can be ascribed to evacuation of water of coordination from the $[\text{Zn}_3\text{Cl}(\text{H}_2\text{O})(\text{PO}_4)_2]^-$ layers with immediate collapse of the structure.

What is the origin of the EG molecules in the structure of NTHU-9 and the filtrates? After examining possible reactions involving choline chloride,^[15] we conjectured that choline underwent hydrolysis (the water content of the DES originates from oxalic acid dihydrate) to produce EG molecules and TMA ions, which also appeared in the filtrates. Further evidence for TMA ions forming from DES was obtained by performing a similar ionothermal reaction without the P source, which afforded transparent crystals of $(\text{TMA})_2\text{ZnCl}_4$,^[16] that is, the TMA ions were generated from DES. These findings firmly establish pathway (2) of Scheme 1 converting choline ions to EG molecules, which partially enter the structure of NTHU-9 and partially remain in the filtrate. This is the first observation of an unusual organic reaction enabled by choline-based DES.

Compound 9-MV is the first metal phosphate lattice incorporating the $[(\text{CH}_3)_2\text{bpy}]^{2+}$ ion, also known as methylviologen dication (MV^{2+}). In most bpy-containing MPOs, the bpy molecules prefer coordination as pillaring ligands^[17] to protonation as a template,^[18] let alone undergoing *N,N'*-dimethylation. When exposed to X-rays ($\lambda = 1.5418 \text{ \AA}$ in powder diffraction measurements), the orange color of 9-MV immediately turned to slate gray (Figure 2), that is, MV^{2+} dications were reduced to $\text{MV}^{\bullet+}$ radicals. The emergence of radicals in 9-MV was confirmed by UV/Vis diffuse-reflectance spectra in which absorption peaks at 398 (sharp) and 620 nm (broad), both characteristic of $\text{MV}^{\bullet+}$ radicals,^[19] appeared after irradiation. Recovery of the orange color on heating the slate gray sample at 200 °C in air for 12 h indicated oxidation of $\text{MV}^{\bullet+}$ radicals back to MV^{2+} dications. This reverse photochromic transformation was almost complete, as

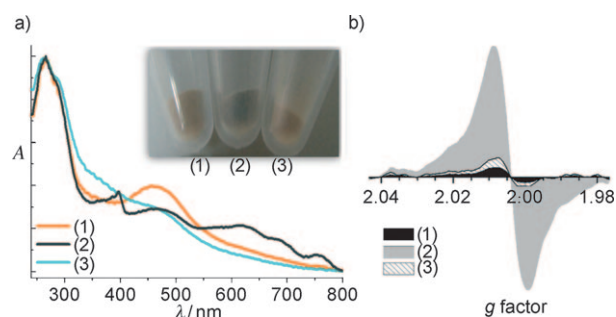


Figure 2. UV/Vis DRS and powder EPR spectra for 9-MV. 1) Original sample. 2) Sample after X-ray irradiation. 3) Irradiated sample after heating.

confirmed by EPR measurements (Figure 2). Compared with other MV^{2+} -containing structures in which reduction to MV^{+} radicals can be readily achieved by UV or visible light, 9-MV required a much higher threshold energy. A possible explanation is the longer charge-transfer pathway of in 9-MV. The charge is assumed to follow the shortest $N\cdots Cl$ path between the MV^{2+} ion and the $[Zn_3Cl(H_2O)(PO_4)_2]^-$ layer, which is 4.83 Å for 9-MV and thus significantly longer than the $N\cdots Cl$ distance of less than 3.5 Å observed for UV-activated photochromic systems.^[20]

Layered compound NTHU-9 is the first metal activator-free orange phosphor material prepared in organically templated metal phosphates. The excitation spectra are strikingly broad, ranging from 350 to 550 nm, and the emission peaks are invariably centered at 600 nm for 9-tmdp and 580 nm for 9-MV (Figure 3). According to our previous investigations on green and yellow luminescent MPOs,^[4,8] the tmdp-type template, when trapped in nanometer-sized channels or pores, is a good sensitizer which, however, plays an additional role in layered NTHU-9. We found that the dark red viscous filtrate also displays orange

emission (Figure S10, Supporting Information). We presumed that a common source of emission might exist in 9-tmdp and its filtrate. We prepared a simulated filtrate by combining EG with the starting materials and found that even a simple mixture of tmdp with EG, after heating at 180 °C (see Experimental Section), gave the same orange emission as the filtrate. Similar phenomena were observed with 9-MV as well. On the basis of these facts we deduced that some “fluorophores” were formed by interaction between EG and tmdp (or bpy) in the simulated filtrates. Such “fluorophores” likewise developed between EG and $[(CH_3)_2tmdp]^{2+}$ ion in 9-tmdp (and between EG and $[(CH_3)_2bpy]^{2+}$ in 9-MV). The amount of “fluorophores” in the solids of 9-tmdp or 9-MV would be diminished due to smaller amount of EG molecules after heating (see aforementioned TG results). This may provide an explanation for the abnormally rapid decay in emission intensity with increasing temperature (see inset of Figure 3).

In summary, we have demonstrated DES synthesis of the first metal-activator-free orange phosphor, NTHU-9, which is a first metal phosphate system with dual photogenerated properties. Moreover, the versatility of DES was discovered to extend to the frequently stable component choline ions, which were shown for the first time to follow two concurrent reaction pathways: one forming methylium ions, which led to *N,N'*-dimethylation of amine templates and formation of a photochromic material, and another affording ethylene glycol, which entered the layered structure of NTHU-9 and endowed it with “fluorophores” responsible for the first observation of orange photoluminescence in organically templated MPOs. Further investigation on the control of choline-based DES as reservoir of methylating agent to prepare novel luminescent and functional materials is in progress.

Experimental Section

9-tmdp was obtained from a reaction mixture of ZnO (0.32 g, 4 mmol), phosphorous acid (0.246 g, 3 mmol), and 4,4'-trimethylenedipyridine (tmdp, 0.4 g, 2 mmol, 98 %) in the DES of choline chloride/oxalic acid dihydrate (20 mmol each), which was heated in a 23 mL Teflon-lined autoclave at 180 °C for 3 d. The product contained single-phase red lamellar crystals of 9-tmdp (yield ca. 86 % based on Zn). By replacing tmdp with 4,4'-bipyridine (bpy, 0.3 g, 2 mmol), we obtained light orange lamellar crystals of 9-MV mixed with brown crystals of $[Zn_3(C_{10}H_8N_2)_4(C_2O_4)_3]$.^[21]

Both reaction filtrates were collected for further characterization and analysis by 1H NMR, ^{13}C NMR, and PL spectroscopy. In the ^{13}C NMR spectra (Figure S8, Supporting Information), chemical shifts other than those of the starting materials were assigned to 2-(dimethylamino)ethanol (DMAE), tetramethylammonium (TMA) ions, and ethylene glycol (EG), which were further confirmed by 1H NMR data. The far smaller signal ratio of choline ions to oxalic acid in the ^{13}C NMR spectra after reaction indicated partial decomposition of oxalic acid to CO_2 . The thus-increased reaction pressure possibly initiated the reactions of choline ions.

For PL measurements, the viscous filtrates were each (0.5 mL) diluted with 3 mL of water, and similar emissions to those of solid samples were observed (Figure S10, Supporting Information). To confirm the assumption that EG might play a role, solutions of amine and EG were heated to simulate the filtrates. An excess of EG (3 mL, 58.8 mmol) was mixed with tmdp (2 mmol) or bpy (2 mmol) and the

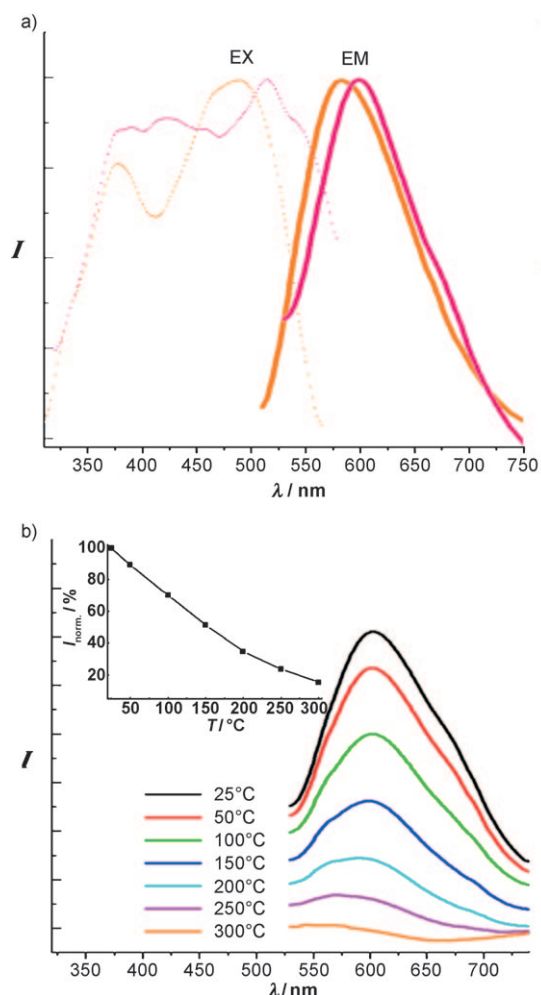


Figure 3. PL spectra for NTHU-9. a) Excitation (dotted lines) and emission curves (solid lines). Red for 9-tmdp excited at 510 nm and orange for 9-MV at 490 nm. b) Temperature-dependent emission curves for 9-tmdp with decay behavior shown in the inset.

mixture heated at 180°C under ambient pressure for 24 h. The resulting solutions had a similar color to the filtrates. Orange emission was therefore inferred to originate by interaction between amine and EG trapped in the solids.

CCDC 765801 (9-tmdp) and 765800 (9-MV) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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