Supporting Information

Novel 3, 6-Unsymmetrically Disubstituted-1, 2, 4, 5-Tetrazines:
S-Induced One-Pot Synthesis, Properties and Theoretical Study

Chen Li, Haixia Ge, BingYin, Mengyao She, Ping Liu,* Xiangdong Li and Jianli Li

Table of Contents

1. A photo of the emission of the tetrazines 4d, 4e, 4f, 4u, 4p, 4q, 4r, 4v in dichloromethane under a UV lamp .................................................................2

2. The calculation of fluorescence quantum yield .................................................2

3. Theoretical calculation .......................................................................................2

  3.1. Computational details......................................................................................2

  3.2. The 3D representation of the Fukui function $f^+(r)$ (positive in red color and negative in green color) and the condensed Fukui function $f^+(r)$ of N and surrounding C atoms of 4a-v .................................................................3

  3.3. The shape of HOMO and LUMO orbitals for the free molecules of 4a-v......6

4. $^1$H NMR and $^{13}$C NMR spectra, IR spectra of all compounds.........................8

1
1. A photo of the emission of the tetrazines 4d, 4e, 4f, 4u, 4p, 4q, 4r, 4v in dichloromethane under a UV lamp

2. The calculation of fluorescence quantum yield

Fluorescence quantum yields ($\Phi_u$) were determined using optically matching solutions of quinine sulfate ($\Phi_f = 0.55$ in 0.05 mol/L H$_2$SO$_4$) as the standard, and the quantum yields were calculated using Equation 1 according to the references.$^{[1, 2]}$

$$\Phi_u = \Phi_f \times \frac{I_u}{I_f} \times \frac{A_u}{A_f} \times \left( \frac{\eta_u}{\eta_f} \right)^2$$  \hspace{1cm} (Equation 1)

Where $\Phi_u$ and $\Phi_f$ are the fluorescence quantum yields of the sample and standard, $I_u$ and $I_f$ are the integrated emission intensities of the spectra for the sample and standard, $A_u$ and $A_f$ are the absorbance of the standard and sample at the excitation wavelength (335 nm and 344 nm, in all cases), and $\eta_u$ (1.4244) and $\eta_f$ (1.33) are the indices of refraction of the sample (dichloromethane) and standard solutions (water), respectively.

References:


3. Theoretical calculation

3.1. Computational details

Gaussian 09 package has been employed for all the calculations.$^{[1]}$ DFT method was exploited to obtain minimum energy structures. The optimized structure is proven to be the local minimum based
on the results of vibration analysis. Fukui function and the atom condensed Fukui function $f'(r)^{[2]}$ based on density functional theory (DFT) have been used to determine the site reactivity and site selectivity. Basis sets of double-$\zeta$ quality (6-31G** for C, H atoms, 6-31+G* for other atoms) are used for the geometry optimization. Theoretical calculation of 4a is based on the crystal structure, and the others are based on simulate molecular structures drawn by Chem3D and GaussView. The single-crystal structure of 4a was determined by X-ray crystallography. CCDC-973196 (for 4a) contains 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.

References:


3.2. The 3D representation of the Fukui function $f^+(r)$ (positive in red color and negative in green color) and the condensed Fukui function $f^+(r)$ of N and surrounding C atoms of 4a-v.
3.3. The shapes of HOMO and LUMO orbitals for the free molecules of 4a-v
4. $^1$H NMR and $^{13}$C NMR spectra, IR spectra of all compounds