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Title: Understanding the effect of an amino group on the selective and ultrafast detection of TNP in water using fluorescent organic probes

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Keywords: Field emission microscopes
Fourier transform infrared spectroscopy
Time-resolved fluorescence
High resolution mass spectrometry

Issue Date: 2018

Publisher: Royal Society of Chemistry

Citation: Journal of Materials Chemistry C, 6(13), pp. 3288-3297

Abstract: We have designed and developed three single-molecule fluorescent probes differing in the number of amino groups, namely 5-((4,6-Diamino-1,3,5-triazin-2-yl)amino)isophthalic acid (H2ATAIA, 1), 5-((4-amino-6-methoxy-1,3,5-triazin-2-yl)amino)isophthalic acid (H2AMTAIA, 2) and 5-((4,6-dimethoxy-1,3,5-triazin-2-yl)amino)isophthalic acid (H2DMTAIA, 3), from cheap and readily available starting materials via simple procedures in high yields for demonstrating their application in highly selective and ultrafast sensing of 2,4,6-trinitrophenol (TNP) in water (slurry mode). Probes 1-3 have been characterized by various analytical techniques, such as melting point, FTIR, UV-vis and NMR (¹H and ¹³C) spectroscopy and high resolution mass spectrometry (HRMS). It is quite evident that the effect of an amino group is more prominent compared to a methoxy group towards the selective detection of TNP over other potentially interfering nitro compounds. The detection limit for the diamino derivative was found to be 120 ppb compared to those with one amino or no amino group (0.8 ppm and 1.2 ppm, respectively). We also report the ideal real time detection of TNP through a contact mode or instant spot via paper strips. Spectral overlap, time-resolved fluorescence studies, quantum yield, Stern-Volmer plots, field emission scanning electron microscopy (FESEM) and DFT calculations have been used to establish their mechanism of action. Furthermore, competitive nitro-analyte tests demonstrate that the selectivity for TNP is more in 1 compared to 2 and 3. To the best of our knowledge, we have demonstrated for the first time molecular decoding of TNP based on the dual read-out identification scheme constructed from life-time and quantum yield. These probes have been found to be highly photostable in the presence of acidic TNP as well as recyclable without much loss of sensitivity up to five cycles. These results vividly depict that these are excellent candidates for environmental monitoring.

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