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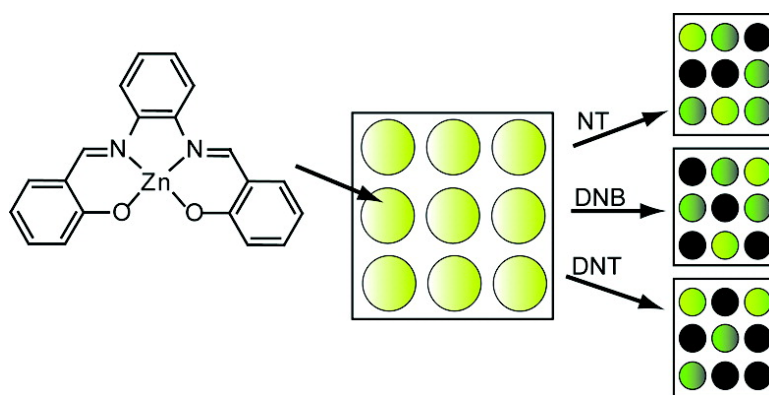
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Discrimination of Nitroaromatics and Explosives Mimics by a Fluorescent Zn(salicylaldimine) Sensor Array

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Identifying and distinguishing related compounds by optical methods is an enormous challenge for chemical sensing. One significant need is to discriminate various plastic explosives, for law enforcement and national security.[1,2] Current sensing methods rely upon the electronic character of nitroaromatics, common components of explosives, for binding[3,4] or chemical reactivity,[2] making discrimination of different nitroaromatics a challenge. Sensor arrays have shown much promise in discriminating odorants[5] and flavorings;[6] however, this requires a family of sensors with differential responses.[7] The Zn(salicylaldimine) (**ZnL**) family provides differential responses to closely related nitroaromatics,[8] and here we organize **ZnL** into a sensor array for the discrimination of explosives mimics and nitroaromatics.
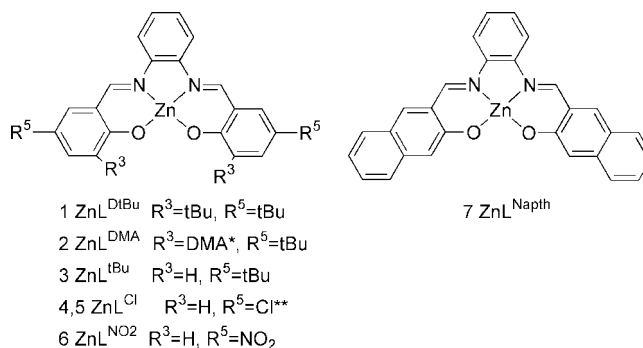
In addition to **ZnL**, conjugated polymers based on phenylene-ethynylene (termed AFPs), polyacetylene,[9] or inorganic polymetalloles[2,4] are efficient optical sensors for nitroaromatics. These polymers are very effective toward nitro compounds that contain π-systems capable of intermolecular stacking with the polymer matrices. AFPs and polymetalloles are less effective toward nitroalkanes, such as 2,3-dimethyldinitrobutane (DMNB). Fluorescence quenching is severely diminished without π-stacking, and efficiency is modest toward nitroaliphatic compound, making discrimination of nitro compounds a challenge for these polymeric sensors.[4]

We have previously reported **ZnL** complexes that are strong fluorophores ($\varphi_{em} = 0.3$)[8a,10] and undergo photoinduced electron transfer with nitroalkanes and nitroaromatics.[8] Electron transfer from the phenolate ring of **ZnL*** to the nitro compound results in fluorescence quenching. Quenching of **ZnL*** is a combination of both static and collisional pathways,[8b] reflecting a delicate balance between the redox potential and steric bulk of **ZnL**. The contribution of each pathway is balanced such that the quenching mechanism depends upon the structures of both **ZnL** and ArNO$_2$.

We have designed a sensor array using seven related **ZnL** fluorophores (Scheme 1), which undergo mixtures of static and dynamic quenching with nitroaromatics. The differential response of each **ZnL** allows the array to discriminate nitroaromatics. These **ZnL** complexes were synthesized as reported previously[8,11] and used at a concentration of 60–200 μM in dry acetonitrile.

Two different experiments were used to train the sensor array: a fingerprinting experiment, in which the concentration of ArNO$_2$ was fixed at 0.12 M, and a classification experiment, in which the ArNO$_2$ absorption was fixed at $A_{300} = 1.0$. Samples were measured in 96-well polypropylene microplates with $\lambda_{ex} = 400$ nm, $\lambda_{em} = 520$ nm. Three plates were analyzed with three readings collected for each plate for a training data matrix of seven **ZnL** complexes $\times$ nine ArNO$_2$ $\times$ nine replicates. The percent quenching was calculated with the equation $(I_0 - I)/I_0 \times 100 = \%$ Quenching, where I_0 is the fluorescence intensity without added quencher.

Scheme 1. **ZnL^R** Fluorophores for Sensor Array

1 ZnL^{DtBu} R^3=tBu, R^5=tBu
2 ZnL^{DMA} R^3=DMA*, R^5=tBu
3 ZnL^{tBu} R^3=H, R^5=tBu
4,5 ZnL^{Cl} R^3=H, R^5=Cl**
6 ZnL^{NO2} R^3=H, R^5=NO$_2$

7 ZnL^{Napth}

*DMA=Dimethylamine
**ZnL^{Cl} is used at low and high concentrations

Quenching of **ZnL** by ArNO$_2$ is controlled by both collisional interactions and by ground-state binding, which lead to a unique fingerprint for each ArNO$_2$ (Figure 1). As an example of how these two mechanisms lead to rich information, **ZnL^{Cl}** could be used both from low concentration (**4**, 16 μM) and from high concentration (**5**, 60 μM) stocks, leading to different responses for each ArNO$_2$ which likely reflect changes in binding interactions. The collective array response was then used to discriminate between structurally similar ArNO$_2$ compounds.

The differential response patterns of the entire array appeared to reflect the physical properties of **ZnL** and ArNO$_2$. The quenching efficiency was enhanced by an increasingly oxidizing ArNO$_2$ compound, which would lead to a thermodynamically more favorable photoinduced electron transfer. The steric bulk and hydrophobicity of both the **ZnL** and the ArNO$_2$ compound affected the quenching efficiency, likely by making the static quenching pathway more favorable. Last, PA and NQ contain Lewis base heteroatoms which could coordinate to the **ZnL**, which may enhance their quenching efficiencies.

To determine the ability of the array to discriminate unknown samples, the classification data were analyzed with linear discriminant analysis (LDA) statistics, due to the large size of the training matrix. The raw data were analyzed using a classical LDA in which all variables were used with a tolerance level set to 0.001.[12] LDA treats the array response as the linear combination of discriminant functions or canonical scores. Discriminant coefficients are defined such that the array response to each ArNO$_2$ is orthogonal, leading to accuracy. Discriminant functions were generated for the data matrix, and only two were needed to provide over 99% of the array discrimination (Figure 2).

The centroids (99%) of each nitroaromatic were distributed in this canonical score plot by chemical structure, reflecting the fingerprinting trends noted above. Mononitroaromatics were separated from dinitroaromatics, and PA and ClAmp were well-

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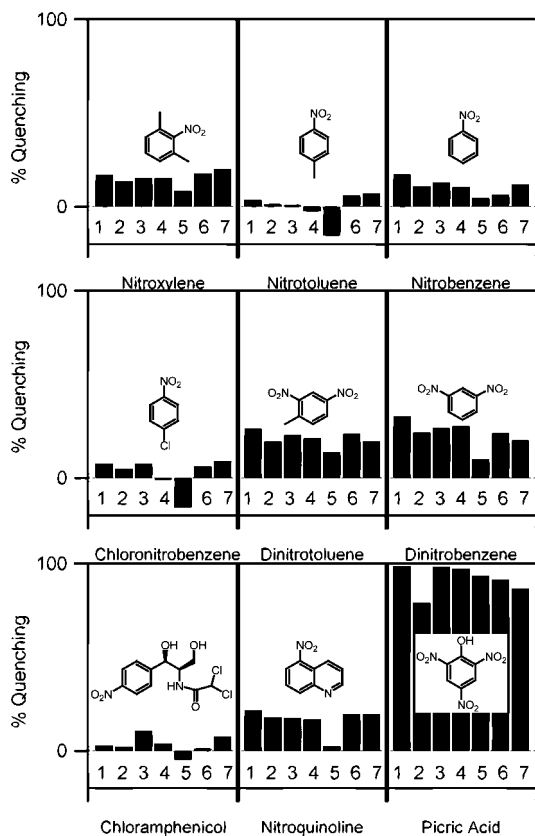
Figure 1. Fingerprints for the nine nitroaromatic quenchers ($A_{300} = 1.00$, dry acetonitrile) in the seven-element **ZnL** array, numbered as per Scheme 1.
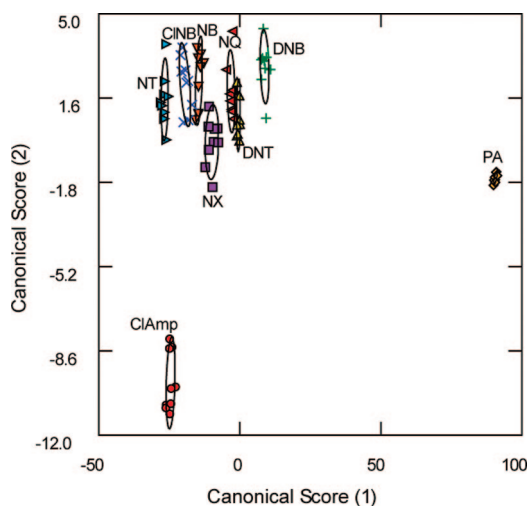
Figure 2. Canonical plot showing the 99% centroids for trained **ZnL** array against nine nitroaromatic analytes; [ArNO₂] normalized, $A_{300} = 1.0$.

separated from the others. Although there are groups that appear to have little separation, this plot defines differences in 2-D space, while LDA discriminates in a multidimensional space. We looked for correlations between these canonical scores and specific physical properties of the nitroaromatics. *Score 1* was linearly correlated with increasing reduction potential ($r^2 = 0.93$), which may explain the distribution by number of nitro substituents. *Score 1* appeared to be a direct reflection of the ease of electron transfer. The linear correlation of *Score 2* with log *P*, a commonly used measure of aqueous solubility, was approximate $r^2 = 0.71$. This thermodynamic parameter reflects both hydrophobicity and polarity, which

indicates the "stickiness" of each nitroaromatic. The rough correlation between log *P* and *Score 2* likely reflected the contribution of static quenching of **ZnL** to the overall array response, which is dependent on the opposing forces of hydrophobiciy and Lewis base character of the quenchers.

The dual quenching mechanisms provided a nice example of how to discriminate analytes such as NT and NB, which differ solely by a methyl group. As both the redox potential and log *P* are similar for these analytes, they could be very difficult to distinguish solely through one quenching mechanism. However, the combination of quenching mechanisms allows the **ZnL** sensor array to discriminate these structurally related nitroaromatics.

Unknown samples were identified according to their canonical scores or their placement in this 2-D space. The array response to each unknown ($A_{300} = 1.00$) was compared with the classification data, and unknowns were identified according to correspondence between their Mahalanobis distances and those of the classified nitroaromatics. The following unknowns were identified with 100% accuracy: DNB, ClNB, ClAmp, NB, and NT.

In summary, we have reported a fluorescence-based sensor array comprising varied Zn(salicylaldimine) complexes which accurately discriminated nitroaromatics. While differential quenching responses for nitro-containing compounds have been reported for polymeric systems, this was largely due to the changes in redox potentials. For example, changing the band gap energy of AFPs altered their quenching efficiency toward nitro compounds.[9] Similarly, quenching response of polymetalloles toward nitroaromatics was correlated with their reduction potentials.[4] As this paper was being submitted, Anslyn et al. published a fluorescence array for broad-class explosives discrimination based on binding interactions with micellar suspensions.[13] The differential quenching of the **ZnL** complexes is distinguished from these examples by their sensitivity to a combination of driving force and aggregation tendency, which permits discrimination within the closely related nitroaromatic structural family.

Supporting Information Available: Sample preparation; training matrices; and canonical score correlations. This material is available free of charge via the Internet at http://pubs.acs.org.

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