A Naked-eye Colorimetric Indicator to Discriminate Aromatic Compounds by Solid-state Charge-transfer Complexation

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A colorimetric indicating system has been developed using solid-state charge-transfer complexation to demonstrate color changes in response to various aromatic compounds and their isomers that provide no color changes under diluted solution conditions.

Color-change observable by the naked eye is the easiest method to detect chemicals and chemical reactions, and has been attracting many chemists to develop qualitative or quantitative analyzing systems accompanied with color changes. Most of the colorimetric indicators are reported to detect metal ions or anions by changes of intermolecular charge-transfer bands of chromogenic signalling units. However, research efforts towards the establishment of qualitative colorimetric indicators for organic compounds are still in infancy.[1–3] Moreover, most of them are performed in solution states, and design of solid-state indicators in the absence of any solvent is still in demand from green-chemistry.[4] Thus, here we wish to report a novel colorimetric indicator for a wide range of aromatic compounds by solid-state formation of charge-transfer (CT) complexes.[3] Solvent-free co-grinding[4,5] of analytes with the indicator provided more vivid color changes in comparison with those in the solution states.

CT complexes[6] in solution have been utilized rarely as chromophores due to their low binding constants,[3] and in the solid state they have attracted growing interest in the recent years.[7,8] Thus, inspired by result of the color-sensing organogels,[9] here we developed a new *indicator* system based on CT complexation in the solid state. We chose a naphthalenediimide (NDI) derivative as the acceptor molecule, because NDI easily forms inclusion crystals with DMF by recrystallization,[10] and does not form one-dimensional columnar structures or π–π stacking structures of naphthalenediimide groups in the crystalline state. In this report, we demonstrate the appearance of colorful CT complexes of NDI with a wide variety of aromatic compounds as summarized in Chart 1 by the solid-state co-grinding technique.[4,5]

The naphthalenediimide (NDI) was synthesized by a reported procedure (ESI).[12] Without any electron-donors, it was slightly yellow-colored powder after recrystallization from DMF followed by drying in vacuo. In a typical experiment, NDI and an aromatic molecule have been taken in a 1:1 molar ratio in the solid state in molten pastern and ground. Within one minute, colors originating from CT complexation were developed. Prolonged grinding for 30 min made the mixture much brighter. The acceptor NDI forms the CT complexes (**1**NDI–**5**NDI) with a series of polyaromatic hydrocarbons (Chart 1); orange-yellow color for **1**, yellow with **2**, gray-green with **3**, dark yellow with **4**, and orange with **5** as shown in Figure 1.

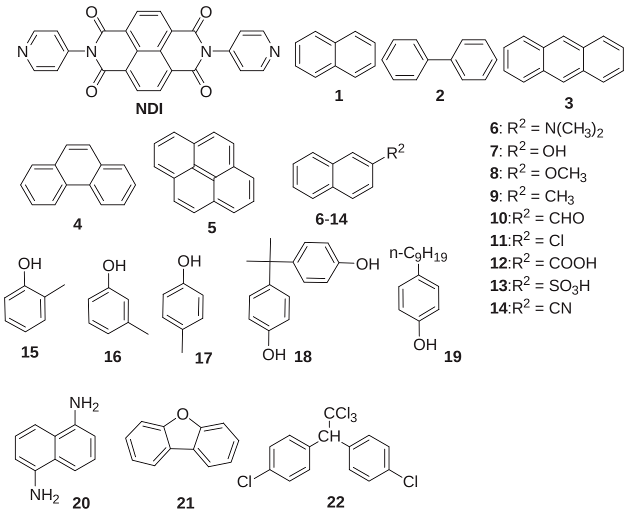

Chart 1. Structures of NDI and analytes used in the present *indicator* system.

Solid-state visible absorption spectra of these complexes indicated that as π-electron conjugation increases, the $\lambda_{\max}$ of the CT complexes also shifts towards higher value. Thus, polyaromatic hydrocarbons can easily be identified by visualization of color changes in the presence of NDI. The identification limit of the analytes by this method was about 1.0 mg ($\approx$0.00625 mmol) of analytes means it can be consider as a qualitative analysis aspect.

Formation of the CT complexes by the solid-state reaction was monitored by X-ray diffractions.[11] For example, the powdered sample of NDI and **5** freshly prepared by mixing in the solid state revealed that the solid-state reaction provides the same crystal structure as that from the solution as shown in Figure 2. After 30 min grinding of NDI and **5** in a 1:1 molar ratio in the solid state, new crystalline morph was observed which is different from the starting materials NDI and **5**, and identical to the simulated diffraction pattern of a single crystal obtained from the solution. The similarity of the product is in contrast to the result reported recently in a similar CT complex formation.[7] In the crystal structure of **5**NDI, the two π-electron planes of NDI and **5** are in close proximity to form the charge-transfer complex between the donor and the acceptor (distance between two π planes is 3.316–3.390 Å). The stacking of the π-electron planes with offset formed one-dimensional columnar assemblies slightly tilting from the perpendicular axis of the π-electron planes.

Since stronger electron donors are expected to form CT complexes more red-shifted $\lambda_{\max}$ in the visible region, and the electron-donating properties of the aromatic donors depend upon the functional groups on the aromatic ring of the donors,

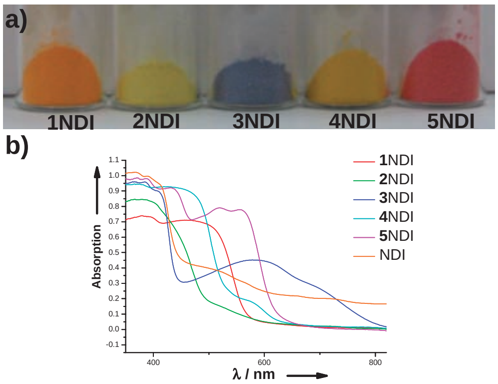

Figure 1. (a) CT complexes of NDI with a series of polyaromatic compounds and (b) their solid-state absorption spectra.

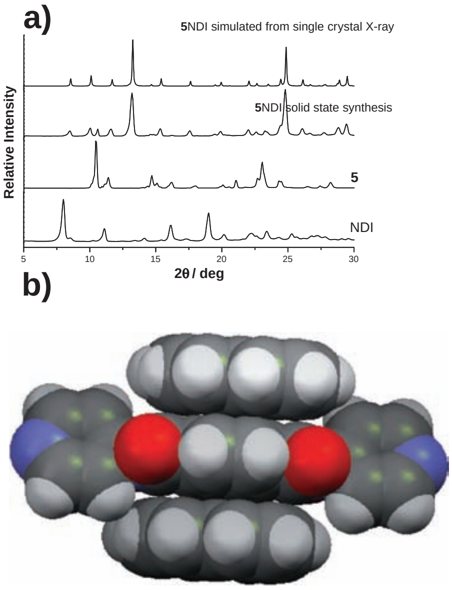

Figure 2. (a) Comparison of XRPD patterns of complex **5**NDI in different crystallization condition, together with **5** and NDI, (b) crystal packing diagram for **5**NDI.

we further investigated the solid-state complexation of NDI with a series of 2-substituted naphthalene (Figure SI1).[12]

It is quite interesting that some aromatic compounds had no obvious color changes in the solution mixtures. The highly concentrated state in the solid-solid co-grinding mixtures should promote the formation of CT complexes and develop vivid colors. Moreover, the absorption maxima of the CT complexes were red-shifted according to increase in the electron-donating abilities, and the present system showed a good correlation of the Hammett constant and $\lambda_{\max}$ of the CT complex in the solid state (Figure SI1).[12] Another important merit of the present *indicator* system is visualization of the differences of the isomers. For examples, co-grinding of NDI with stoichiometric amount of *o*-, *m*-, and *p*-cresol present as a liquid at room temperature, provided the CT complexes with the different colors which can be easily visualized by the naked eye. Moreover, solid-state grinding of molecule NDI to form CT complexes could be applicable for liquid donors. Finally, the most important aspect for this system is applicability to a wide range of toxic aromatic pollutants such as potent endocrine disruptors and some model compounds of persistent organic pollutants. Bisphenol A (**18**), 4-nonylphenol (**19**), 1,5-diaminonaphthalene (**20**), and dibenzofuran (**21**) can be identified by different color CT complex formation with acceptor molecule NDI, as shown in Figure SI2.[12] It is important to mention that in the present studies, acceptor NDI did not form a CT complex with well-known toxic chemical DDT (**22**).

In summary, the use of simple solid-state co-grinding combined with CT complexation allows remarkable qualitative colorimetric recognition of a vast range of aromatic molecules by the naked eye. The solid-state co-grinding[5] with aromatic liquids and solids easily provided solvent-free highly concentrated conditions that promote the formation of the CT complexes with brighter color changes than those in the solution and gel state. Thus, for the first time, solid-state CT complexation enables us to demonstrate the color changes in response to various aromatic compounds that provide no color changes under the diluted solution conditions. Combinatorial approaches or two-dimensional array[1c,13] by changing acceptor molecules should provide more accurate identifying tools for isomers of more complicated aromatic compounds and other organic molecules with an aromatic ring including highly toxic and environmental pollutants and regulated narcotics are currently underway in our laboratory.

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11 Crystal data for **5**NDI (CCDC 662775) at 298 K: $C_{40}H_{22}N_4O_4$, Triclinic $P\bar{1}$, $a = 7.9274(16)$ Å, $b = 9.1680(19)$ Å, $c = 10.337(2)$ Å, $\alpha = 89.515(4)^\circ$, $\beta = 88.543(4)^\circ$, $\gamma = 72.661(5)^\circ$, $V = 716.9(3)$ Å^3, $Z = 2$, $d_{\text{calcd}} = 1.442\,\text{g}\,\text{cm}^{-3}$, 3269 reflections measured, 1459 unique reflections. Final $R_1 = 0.0476$ and $wR_2 = 0.1267$. This crystallographic data have been deposited with CCDC as no. 662775. Copy of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or as ESI on the CSJ journal website.[12]

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