



Nickel–sodium pyrene tetrasulfonic acid based co-ordination polymer as fluorescent template for recognition of azo dyes



Darsi Rambabu, Chullikkattil P. Pradeep, Abhimanew Dhir*

School of Basic Sciences, Indian Institute of Technology, Mandi 175001, Himachal Pradesh, India

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ABSTRACT

Pyrene tetrasulfonic acid based co-ordination polymer (**Na–Ni–PTS**) with nickel and sodium as metal ions is synthesized. The fluorescent polymer **Na–Ni–PTS** is utilized as template for recognition of industrially relevant azo dyes BY (Brilliant yellow), AYGG (Alizarin yellow GG), MO1 (Mordant orange 1), TONa (Tropaeolin O sodium salt), MO (Methyl orange), PAP (4-Phenylazophenol), SII (Sudan II), OG (Orange G), AB (Azobenzene). It was observed that most of the azo dyes quenched the fluorescence **Na–Ni–PTS**. The practical application of **Na–Ni–PTS** as azo dye sensor was observed using a fabric on which BY was absorbed and also by mixing of BY with food stuff.

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1. Introduction

Recently, interests of chemists to design and synthesize new co-ordination polymers (CPs) with different dimensions and topologies have classified CPs as new class of materials with wide variety of applications [1–8]. These materials have been reported for their potential applications in photoluminescence, catalysis, gas storage and biological science [2–6]. In addition to this, CPs with fluorescent organic linkers has drawn much more attention due to their applications in light emitting display devices and as chemical sensors [7,8].

Our research focuses on development of new organic and organic-inorganic hybrid materials for diverse applications [9–14]. In this context, we reported cadmium based co-ordination polymer as synthetic blood plasma anticoagulant [13]. We also reported a co-ordination polymer protein composite for anion sensing application [14]. In continuation of our research work and keeping in view the significance of fluorescent CP, now we have synthesized new nickel sodium CP **Na–Ni–PTS** with pyrene tetrasulfonic acid as organic linker.

Pyrene is well known for its fluorogenic properties which are widely used in sensing applications [15–17]. PTS (1,3,6,8-pyrenetetrasulfonic acid tetra sodium salt) is substituted pyrene

derivative and a well-known solid state organic functional material. Its electron rich donating nature and the characteristic structural feature of having four sulfonate functional groups in four different directions make it a very potent molecule [18,19]. Therefore, it has been investigated for various applications ranging from pharmaceutical drug delivery to food and cosmetics [20–22]. PTS is also utilized for the formation of hydrotalcite-like compounds (also known as layered double hydroxides (LDH) or anionic clays) which are used in industrial applications like catalysts for oxidation, reduction and separation processes [23]. Recently, Wei et al. reported double layered hydroxide (LDH) ultrathin films prepared by alternate deposition of PTS and metal–metal LDH nano-sheets, which were utilized for the fluorescence chemo sensing application [24].

In the present manuscript, fluorescent polymer **Na–Ni–PTS** is utilized as template for recognition of industrially relevant azo dyes *i.e.* BY (Brilliant yellow), AYGG (Alizarin yellow GG), MO1 (Mordant orange 1), TONa (Tropaeolin O sodium salt), MO (Methyl orange), PAP (4-Phenylazophenol), SII (Sudan II), OG (Orange G) and AB (Azobenzene). During the textile process, inefficiency in the coloring generates large amounts of dyes residues which are directly released into water bodies consequently contaminating the environment [25–34]. Among the various residues of dyes that pollute environment important ones are azo dyes. The azo dyes are highly toxic, carcinogenic and genotoxic because of their high Chemical Oxygen Demand (COD) values [25]. Therefore, recognition of these dye molecules is highly significant. To the best

* Corresponding author. Tel.: +91 905 237912; fax: +91 905 237924.
E-mail address: abhimanew@iitmandi.ac.in (A. Dhir).

of our knowledge, use of PTS based CP as template for recognition of azo dyes is unprecedented.

2. Experimental

2.1. Synthesis and characterization of Na–Ni–PTS

A mixture of pyrene tetrasulfonate-sodium salt hydrate (PTS), 0.0305 g (0.05 mmol) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.015 g) (0.05 mmol) in 3 ml of DMF were placed in acid digestion bomb and was heated in oven at 150 °C for 72 h. The mixture was allowed to cool overnight at room temperature to obtain yellow colored crystals (0.027 g, yield 42.2%) which were washed with DMF (3 × 1 ml) and were dried under vacuum at room temperature.

2.2. Samples preparation

For all analytical experiments, 10 mg of Na–Ni–PTS was dispersed in 100 ml H_2O , buffered with HEPES (pH = 7.4), Conc. 0.078 mM (using formula weight from crystal data). For comparative studies, same amount of PTS (10 mg) was dissolved in 100 ml water (pH 7.4), Conc. 0.164 mM. The stock solutions (1 mM) of all azo dyes was prepared either in distilled water (BY, AYGG, MO, MO1, OG and TONa) or in absolute alcohol (PAP, SII and AB).

3. Results and discussion

3.1. Description of Na–Ni–PTS crystal structure

The compound Na–Ni–PTS crystallizes in monoclinic $I2/c$ space group. The asymmetric unit consists of half of the PTS^{4-} unit, half of a $[\text{Ni}(\text{DMF})_2(\text{H}_2\text{O})_4]^{2+}$ complex (where Ni and two water oxygens are in special position), one Na and three DMF molecules (Fig. 1 and Fig. S1).

The crystal structure and refinement data are presented in Table 1. In the crystal structure, the Na center is coordinated to 4 DMF units and 2 PTS^{4-} units, thus exhibiting octahedral coordination geometry. The two PTS^{4-} units coordinate to Na through two sulfonate groups as shown in Fig. 2A. The observed $\text{Na}(\text{I}) \cdots \text{O}$ bond lengths vary between 2.312 and 2.471 Å, which are comparable to similar values reported earlier [35–38]. The $\text{Ni}(\text{II})$ center is coordinated to two DMF molecules and four water

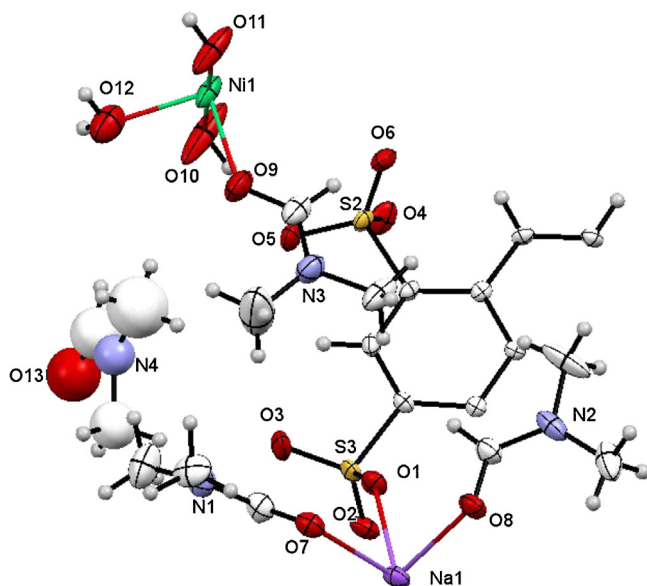


Fig. 1. Asymmetric unit of Na–Ni–PTS (ORTEP diagram).

Table 1
Crystal data and refinement parameters for Na–Ni–PTS.

	Na–Ni–PTS
Empirical formula	$\text{C}_{40}\text{H}_{70}\text{N}_8\text{O}_{24}\text{S}_4\text{Na}_2\text{Ni}$
M (g/mol [−])	1279.97
T (°K)	150.00(10)
Wavelength	1.54184 Å (Cu)
Crystal system	Monoclinic
Space group	$I2/c$
a (Å)	25.4766(7)
b (Å)	7.1710(3)
c (Å)	31.5592(10)
α and γ (deg)	90
β (deg)	90.31
V (Å ³)	5765.6(3)
Z	4
D_{calcd} (Mg/m ³)	1.475
μ (mm [−])	2.723
$F(000)$	2688
Crystal size (mm ³)	0.134 × 0.119 × 0.049
2θ theta range (deg)	6.94 to 133.16
Reflections collected	9753
Independent reflections	5070 [$R_{\text{int}} = 0.0228$]
Absorption correction	Gaussian
Max. and min. transmission	0.892 and 0.760
Refinement method	Least-squares on F^2
Data/restraints/parameters	5070/0/354
S	1.064
Final R_{int} [$I > 2$ sigma(I)]	$R_1 = 0.0673$, $wR_2 = 0.1920$
R_{int} (all data)	$R_1 = 0.0751$, $wR_2 = 0.2007$

molecules in an octahedral fashion resulting in a centrosymmetric $[\text{Ni}(\text{DMF})_2(\text{H}_2\text{O})_4]^{2+}$ complex as shown in Fig. 2B. The observed $\text{Ni} \cdots \text{O}$ bond distances of this complex are comparable to that of similar $\text{Ni}(\text{II})$ complexes reported earlier (Table S1) [38].

All the 6 ligands coordinated to the Na center act as bridging ligands and connect each Na center to its neighboring two Na centers in a centrosymmetric manner as shown in Fig. 3. The Na_3 unit thus formed by connecting each Na to two of its neighboring Na centers in a centrosymmetric manner through two bi-dentate sulfonate ($\mu_2\text{-}\eta^2$) bridges (Through O1, O2#2 and O2, O1#3) and four bi-dentate DMF bridges (Through O7, O8 and O7#2, O8#2) is shown in Figs. 3 and 4 and Fig. S2. In this unit, the $\text{Na} \cdots \text{Na}$ distance is 3.597 Å. This mode of bridging leads to the generation of 1-D chain like arrangement of Na centers along the b -axis (Fig. 4). The bridging DMF molecules arranged in between two PTS^{4-} layers (having pyrene–pyrene centroid to centroid distance of 7.171 Å) exhibit weak $\text{C}–\text{H}(\text{DMF}) \cdots \text{Pi}(\text{PTS}^{4-})$ interactions (Table S3 and Fig. S3) with the PTS^{4-} moieties. These 1-D chains of Na centers along the b -axis are inter-connected by bridging PTS^{4-} units resulting in a 2-D network as shown in Figs. 3 and 4 and Fig. S2. Out of the four sulfonate (SO_3^-) groups present on each PTS^{4-} units, only two sulfonate groups are involved in bonding with Na metal centers. The remaining two sulfonate groups remain free of any bonding interactions with Na centers. Na–Ni–PTS has thus an anionic 2-D coordination network, which is charge balanced by the inclusion of cationic $[\text{Ni}(\text{DMF})_2(\text{H}_2\text{O})_4]^{2+}$ complexes in the crystal lattice. The 2-D network formed from the Na metal centers and the coordinated DMF and PTS^{4-} units, is extended into a 3-D framework assembly through four $\text{O}–\text{H} \cdots \text{O}$ hydrogen bonding interactions ($\text{O12}–\text{H} \cdots \text{O6}\#1$, $\text{O12}–\text{H} \cdots \text{O4}\#2$, $\text{O11}–\text{H} \cdots \text{O5}\#2$ and $\text{O10}–\text{H} \cdots \text{O5}$) between the anionic 2-D network and the cationic $[\text{Ni}(\text{DMF})_2(\text{H}_2\text{O})_4]^{2+}$ complex (Fig. 5). In these H-bonding interactions, water $\text{O}–\text{H}$ groups attached to the $\text{Ni}(\text{II})$ center act as the donors while the oxygens from the free SO_3^- groups act as the acceptors. The relevant parameters are shown in Table S4 and Fig. S4. Thus, in the packing view of Na–Ni–PTS, anionic 2D networks $[\text{Na}_2(\text{PTS}^{4-})_n(\text{DMF})_4]^{2-}$ and the cations $[\text{Ni}(\text{DMF})_2(\text{H}_2\text{O})_4]^{2+}$ are arranged alternatively Fig. 5. This type of arrangement is typical

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