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Terpyridine-based smart organic–inorganic hybrid gel as potential dye-adsorbing agent for water purification

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Abstract

A terpyridine-based organic–inorganic hybrid gelator possessing triethoxylsilane moiety was synthesized and its adsorption capacity for aromatic dyes in the absence and the presence of metal ions such as Zn^{2+} and Cu^{2+} was measured by UV–vis spectroscopy. From aqueous solutions of dyes, the hybrid gel, in the absence of metal ions, adsorbed 97.4% for basic blue 41, 94.2% for crystal violet, and 41.5% for bromocresol green. When metal ion was present, the adsorption capacity of dried hybrid gel **1** for the anionic dye bromocresol green significantly increased due to the enhanced electrostatic interaction between cationic gel and anionic dye. Thus, this hybrid gel can efficiently adsorb various toxic dyes in water.

Keywords: Adsorption capacity; Dye-adsorbing agents; Gelator; Hybrid gel

The utilization of various adsorbents to remove organic or heavy metal pollutants from wastewater is a very prominent subject of research. Besides the classical activated carbon filters, other materials that have been recently studied include typical natural or treated clays,[1–3] organically modified synthetic porous silica,[4–6] three-dimensional cross-linked polymers,[7,8] and dendritic polymers.[9,10] A common characteristic of these materials is their hydrophilicity, so that they effectively interact with water. However, hydrophilic materials are poor adsorbents for organic pollutants. For this reason, they must contain hydrophobic regions, which can accommodate and retain organic substances. Most organic polymers, such as hydrogels or dendritic polymeric structures as well as block copolymers, have the capacity to form both hydrophilic and hydrophobic domains.

Recently, pollutants, including water-soluble toxic dye molecules, have been removed from wastewater using organogel scaffolds. For example, Lianos and co-workers[11–14] have reported that an organic–inorganic hybrid gel was a very effective agent to remove toxic dyes from water. Although hydrogels and organogels have been studied extensively,[15–19] a few examples of organic–inorganic hybrid gels, which can adsorb organic toxins have been described.[6,11,20]

With those objectives in mind, we have designed and synthesized the organic–inorganic hybrid gelator **1** (Fig. 1 and Scheme S1).[21] The triethoxylsilane group was introduced as the hydrophilic moiety. Particularly, the triethoxylsilane group plays an important role in the gel state to create the silica network on the siloxane. However, the polycondensation reaction of triethoxylsilane moiety does not act as a driving force for gel formation. The hydrophobic terpyridine group acts as a driving force to adsorb aromatic organic molecules from the water phase and as binding site for metal ions. In addition, the urea moiety

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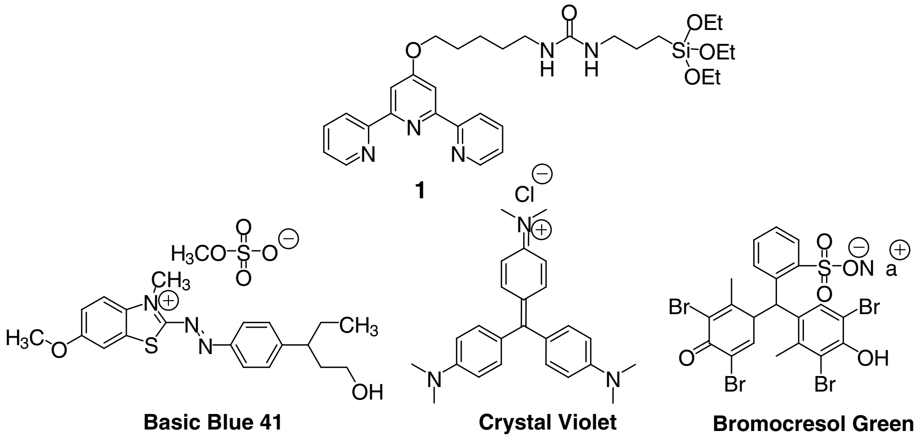

Fig. 1. Chemical structures of gelator **1** and various dyes used in this work.

acts as the main driving force for the gelation of **1** by intermolecular hydrogen bonding interaction. Here, we report the formation of an organic–inorganic hybrid gel using terpyridine-based gelator **1** containing urea residues as intermolecular hydrogen bonding site and the dye adsorbing the efficient removal of different types of water-soluble dyes from contaminated water.

The organic–inorganic hybrid gelator **1** was synthesized, purified, and characterized, and its gelation ability was studied without or with $CuCl_2$ and $ZnCl_2$ to investigate the adsorption capacity for ionic aromatic dyes. To test gelation, **1** and a solvent were heated in a sealed glass tube until the solid dissolved and then cooled to room temperature (Table S1). Successful gelation was manifested by the absence of observable flow when a sample is inverted. Commonly, the terpyridine-based gelator **1** showed two 'G' (stable gel) marks in acetonitrile and acetone, two 'PG' (partially gel) marks, one 'I' (insoluble) marks and three S (soluble) marks, indicating that **1** act as a versatile gelator of various organic solvents. Particularly, **1** revealed good gelation ability in aprotic solvents (Fig. 2a). Also, in these solvents, the gelation ability of gelator **1** in the presence of Cu^{2+} and Zn^{2+} ions was similar to that of the results without metal ions.

SEM image of xerogel **1** derived from acetonitrile gel **1** revealed fibers with 16–20 nm diameter and lengths of several micrometers (Fig. 2b). FT-IR spectroscopy gave more detailed information about the self-assembled structures (Fig. S1). In the FT-IR spectrum of the acetonitrile gel, characteristic peaks appeared at 3340 and 1628 cm^{-1}, which were assignable to N–H and C=O stretching vibrations, respectively. These signals are indicative of strong intermolecular H-bonding interactions between urea groups, and are quite similar to absorbances seen in the solid-state (1630 cm^{-1}). In acetonitrile solution, however, the stretching urea NH bands of gelator **1** appeared at 1650 and 1634 cm^{-1}, indicating that the strong H-binding networks formed in the gel state are disentangled in the solution-state. Furthermore, after gel formation, new peaks of gel **1** appeared at around 3600 cm^{-1} for –SiOH and 1070 and 788 cm^{-1} for –Si–O–Si–. These findings support the view that gel **1** was polymerized by hydrolysis and condensation that occurred during the gel state. Hybrid gel **1** was not thermally reversible because the polycondensation reaction thermally stabilized the structure of hybrid gel **1**.

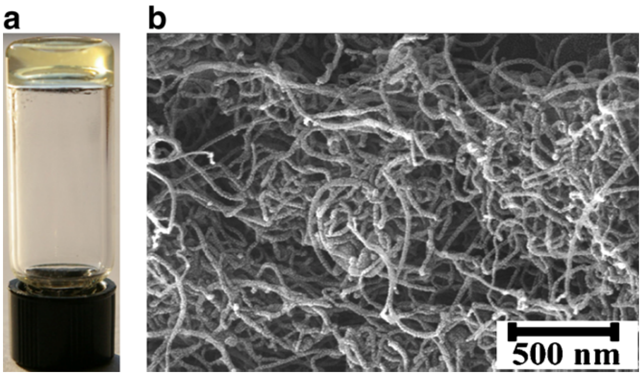

Fig. 2. (a) Picture and (b) SEM image of hybrid gel **1**.

In a given amount, the capacity of the gel to adsorb various dyes was quantitatively estimated (Table 1). When a solution of basic blue 41 was added to dried hybrid gel **1**, the color of **1** changed from white to blue within a few hours (Fig. 3a). The adsorption capacity for dyes using the dried gel without metal ion was studied by UV–vis spectroscopy. After addition of dried hybrid gel to the dye solution, the intensity of the absorption maxima of the dye solution decreased over time, and after 30 h it almost disappeared (Fig. 3b and c). This indicates the adsorption of dye molecules by the surface of the gel. These results explained that the ionic aromatic dyes may be adsorbed by π–π stacking between the terpyridine unit of **1** and the aromatic dye molecule.[22] Also, as mentioned above, the polycondensation reaction of $Si(OEt)_3$ segments possibly contributed the stabilization of the gel structure after adsorption of the aromatic dyes.

In the absence of metal ions, the capacities of the hybrid gel to adsorb dyes from aqueous solutions were determined to be 97.4%, 94.2%, and 41.5% for basic blue 41, crystal violet, and bromocresol green, respectively (Figs. S2–S4).

Table 1
Adsorption data of dried hybrid gel **1** without and with metal ions for various dyes

Dye	λ_{max} (nm)[a]	Gel **1**		Gel **1** + Cu^{2+}		Gel **1** + Zn^{2+}	
		Adsorbed amount (mg/g)[b]	% Removal	Adsorbed amount (mg/g)	% Removal	Adsorbed amount (mg/g)	% Removal
Basic blue 41	615	141.0	97.4	115.7	86.5	86.9	91.1
Crystal violet	582	115.7	94.2	89.7	73.3	92.6	75.6
Bromocresol green	614	86.9	41.5	159.0	77.5	162.1	74.2

[a] Wavelength of light absorption maximum.

[b] Quantities of the adsorbed dye per gram of the adsorbent.

These results indicate that the noncharged hybrid gel preferentially adsorbs cationic dye molecules such as basic blue 41 and crystal violet. In contrast, the addition of metal ions significantly increased the adsorption capacity of the dried hybrid gel **1** for the anionic dye, bromocresol green due to the enhanced electrostatic interaction between the cationic gel and the anionic dye. However, the presence of metal ion decreased the adsorption capacity of dried hybrid gel **1** for cationic dyes (basic blue 41 and crystal violet) due to the repulsion between cationic gel **1** and the cationic dye. In addition, the dried hybrid gel **1** adsorbs ionic dyes such as crystal violet, basic blue 41, and bromocresol green more efficiently than pyrene (a nonionic dye, <5.0%). These results indicate that gel **1** can efficiently purify and separate of ionic dyes from water. Furthermore, the gel remains stable for several months after adsorption of dye molecules.

The TEM image of gel **1** after adsorption of dye depicts fibers with 50–100 nm diameter and several micrometers in length (Fig. 3d). The increased size of gel fiber **1** after exposure to dye molecules verified the efficient adsorption of the dye molecules.

IR spectroscopy confirmed the adsorption of dye molecules. In the spectrum of the free gel, absorbance bands appeared at 3382, 2975, 2948, 1656, 1634, and 1614 cm^{-1} whereas in the spectrum for the basic blue 41-adsorbed gel **1**, absorbance peaks appeared at same positions as well as additional signals at 1206, and 1076 cm^{-1} (Fig. S5). The new peaks originated from the basic blue 41, giving solid evidence that the basic blue 41 molecules were adsorbed in the gel phase.

Proton NMR studies provided further information about adsorption of basic blue 41 in the dried gel phase. We obtained the ^1H NMR spectrum of dried gel sample **1** after adsorption of basic blue 41 (Fig. S6). Interestingly, there were two resonances in the aromatic regions, which correspond to the gelator and a new species. New peaks

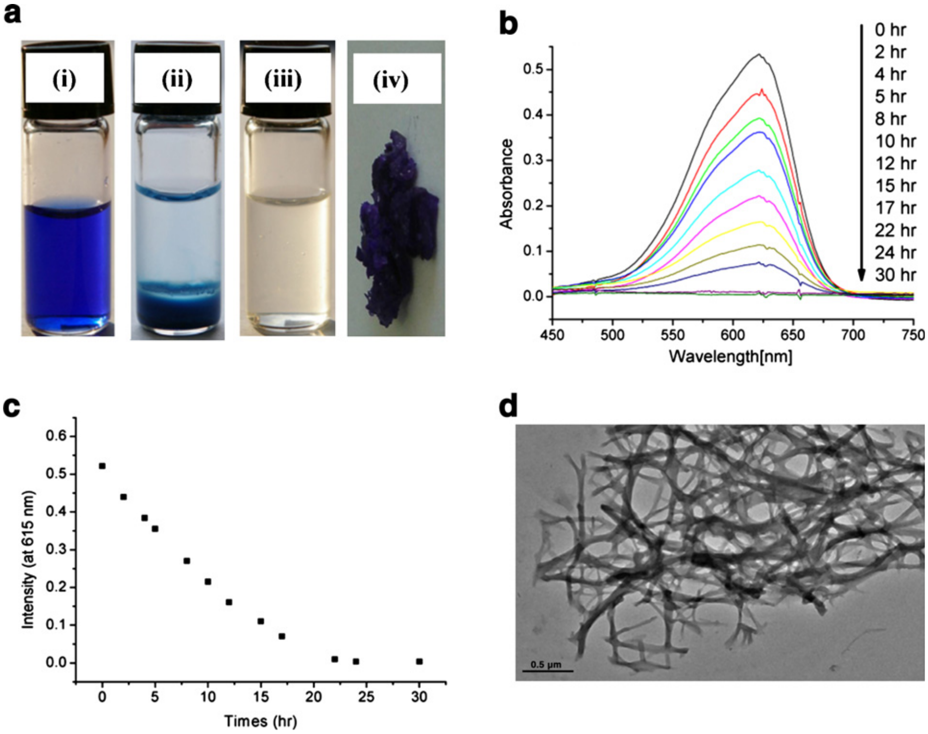

Fig. 3. (a) Picture of (i) basic blue 41 solution, (ii) basic blue 41 solution + dried hybrid gel, (iii) basic blue 41 solution after removal of dried hybrid gel from (ii), and (iv) basic blue 41-adsorbed gel. (b) Time-dependent UV–vis spectra of basic blue 41 solution after addition of the dried hybrid gel. (c) Absorbance changes of basic blue 41 solution upon the addition of the dried hybrid gel. (d) TEM image of the basic blue 41-adsorbed gel.

appeared at 8.21–8.15, 7.75, and 7.30–7.25 ppm. These peaks originated from basic blue 41, indicating that the basic blue 41 molecule is efficiently adsorbed in the gel phase. In addition, we confirmed that 97 mol % of basic blue 41 in the water phase was extracted into dried gel **1** phase according to the integration ratio of the ^1H NMR spectrum.

In conclusion, we report the adsorption behavior of a self-assembled organic–inorganic hybrid gel. The self-assembled organic–inorganic hybrid gel is very efficient as an adsorbent of dyes from aqueous solutions. A cationic dye, basic blue 41 in aqueous solution phase is most efficiently adsorbed into organic–inorganic hybrid gel **1** phase. Furthermore, the adsorption capacity of gel **1** is modulated by the presence of metal ion. This organic–inorganic hybrid gel is one candidate for technological applications in environmental field.

Acknowledgments

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Supplementary data

FT-IR spectra of solution **1** and gel **1**, UV–vis spectra and NMR spectra of **1** by addition of dyes, experimental section. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.11.212.

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21. *Compound* **1**. To a stirred solution, 0.58 g (1.73 mmol) of 2,2′:6′,2″-terpyridine amine in 30 mL of $CHCl_3$, 0.51 g (2.08 mmol) of 3-(triethoxysilyl)propyl isocyanate was added and the reaction mixture was refluxed for 12 h under the nitrogen atmosphere. The solvent was evaporated and then poured into 30 mL of distilled water. The aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and evaporated in vacuo to give 0.74 g (74%) of **1**. Mp 91.5 °C; ^1H NMR ($CDCl_3$) δ 8.69 (d, 2H, ArH, $J = 4.8$ Hz), 8.62 (d, 2H, ArH, $J = 7.8$ Hz), 8.00 (s, 2H, ArH), 7.85 (t, 2H, ArH, $J = 7.5$ Hz), 7.34 (m, 2H, ArH), 4.72 (t, 1H, NH, $J = 5.7$ Hz), 4.60 (t, 1H, NH, $J = 5.4$ Hz), 4.22 (t, 2H, $–CH_2–$, $J = 6.3$ Hz), 3.81 (q, 6H, $–CH_2–CH_3$, $J = 7.2$ Hz), 3.20 (s, 4H, $–CH_2–CH_2–$, $J = 6.9$ Hz), 1.87 (m, 2H, $–CH_2–CH_2–$), 1.58 (m, 6H, $–CH_2–CH_2–$), 1.22 (m, 9H, $–CH_3$), 0.65 (m, 2H, $–CH_2–CH_2–Si–$); ^{13}C NMR ($CDCl_3$) δ 167.19 ($–C{=}O$), 158.36, 156.98, 156.08, 148.94, 136.80, 123.80, 121.34, 107.34 (Ar), 67.94, 58.38, 42.89, 40.30, 29.91, 28.64, 23.59, 23.38 ($–CH_2–$), 18.26 ($–CH_3$), 7.54 ($–CH_2–Si$); IR (KBr) 3235.9 (NH), 3135.4, 3051.0 (ArH), 2973.6, 2931.4, 2868.1, 1621.0 (CO) 1576.5 (NH); MS (FAB-MS) m/z 581.40 (calcd 581.78).
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