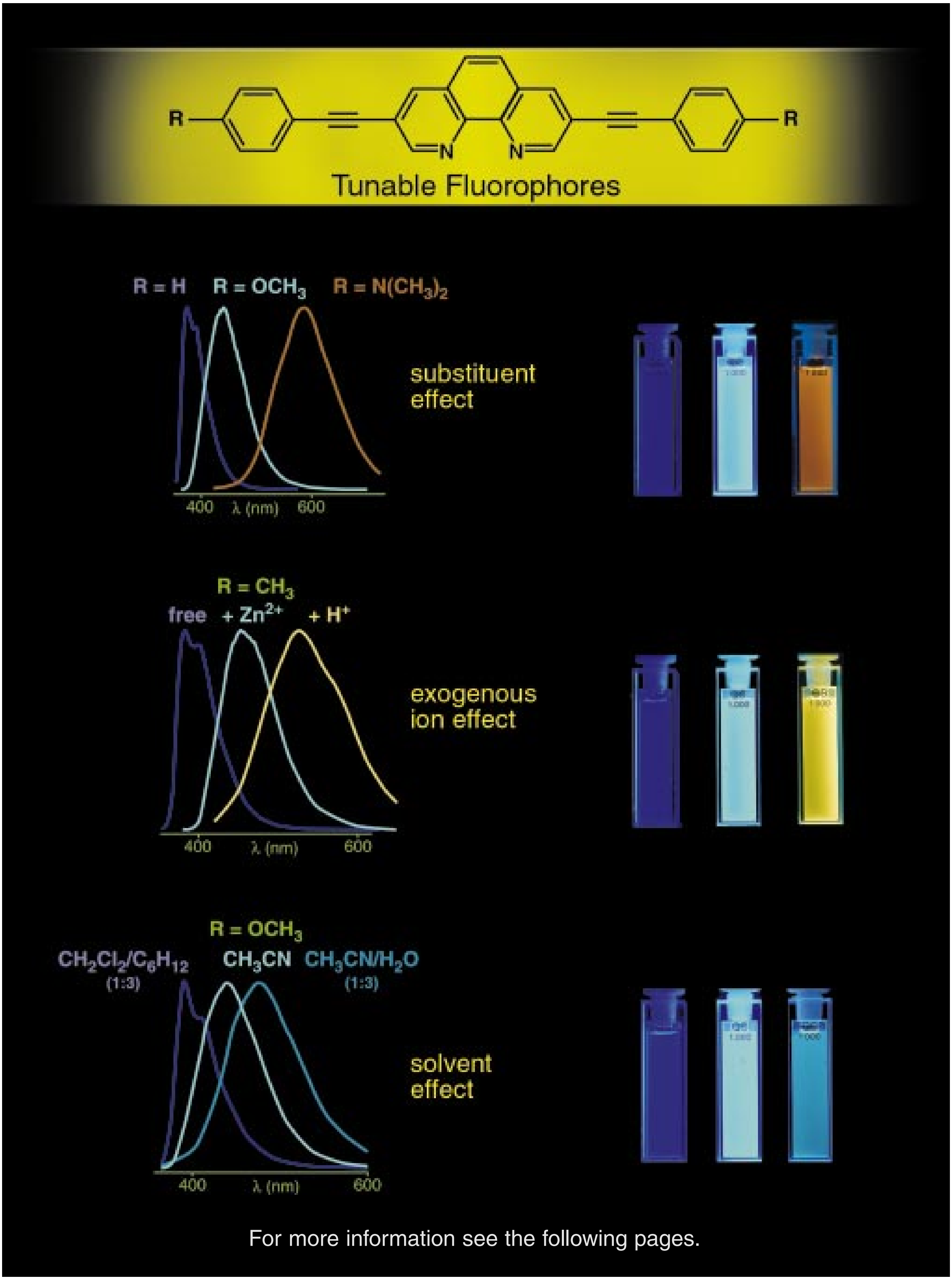


For more information see the following pages.

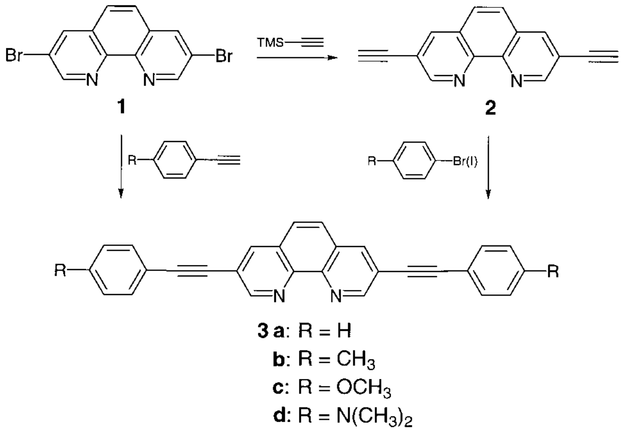
Conjugated 1,10-Phenanthrolines as Tunable Fluorophores**

Hima S. Joshi, Ramin Jamshidi, and Yitzhak Tor*

One of the most exciting developments in molecular electronics is the utilization of organic materials for optoelectronic applications, particularly light-emitting devices.[1] A critical element in designing and fabricating such materials is the control of their emission wavelength.[1c] Conjugated oligomers and polymers, such as poly(*p*-phenylene vinylene) and polythiophenes, permit color tuning through changes in their length, substitution, regioregularity, and degree of conjugation.[1c–3] An alternative approach for controlling the emitted color of organic materials is to append fluorescent chromophores to a polymeric backbone or to blend such dyes into inert polymeric matrices.[4] Ideally, one would like to utilize one family of modular chromophores and tune their photophysical characteristics at will. Herein, we present a novel family of highly fluorescent 1,10-phenanthrolines. The emission wavelength of any derivative is dictated by the nature of its substituents and can be further modulated by exogenous additives such as protons or metal ions. Thus, the same derivative can be utilized for the generation of multiple emission colors.

The rigid framework of 1,10-phenanthroline and its high affinity toward various cations are attractive features for the construction of tunable chromophores.[5] Unfortunately, the parent 1,10-phenanthroline possesses a low fluorescence quantum yield ($\phi_F \leq 0.01$) and a rather short emission wavelength ($\lambda_{em} \approx 360$ nm).[6] Since the most intense electronic transition of the 1,10-phenanthroline skeleton is polarized along the 3–8 positions,[7] we hypothesized that increasing the conjugation along this axis may provide highly fluorescent derivatives with emission in the visible range. Acetylenic linkages are attractive candidates for this purpose as they have previously been shown to effect substantial electron delocalization in the excited state of conjugated arenes and provide intensely fluorescent chromophores.[8] For example, substituting anthracene ($\lambda_{em} = 388$ nm, $\phi_F = 0.25$ in benzene) with two phenylethynyl groups at the 9 and 10 positions results in a 100 nm red-shift in the emission wavelength and extremely enhanced fluorescence intensity ($\lambda_{em} = 486$ nm, $\phi_F = 0.96$).[8] In contrast, direct substitution with phenyl rings to give 9,10-diphenylanthracene, while improving fluorescence quantum yield, produces only a moderate shift in emission wavelength ($\lambda_{em} = 407$ nm, $\phi_F = 0.84$ in benzene).[8] We have therefore targeted 3,8-bis(arylethynyl)-1,10-phenanthrolines **3** as our novel fluorescent chromophores.

Two complementary routes have been utilized for the synthesis of **3**: a) cross-coupling reactions of 3,8-dibromo-1,10-phenanthroline (**1**) with substituted phenylacetylenes, or b) cross-coupling reactions of 3,8-diethynyl-1,10-phenanthroline (**2**) with substituted halo arenes (Scheme 1).[9-11] Both approaches are applicable to most derivatives; however, when an unstable or highly volatile alkyne is required for route (a), the route (b) is preferred.



Scheme 1. Synthesis of conjugated 1,10-phenanthrolines **3** by Pd-mediated cross-coupling reactions. TMS = trimethylsilyl.

Figure 1 shows normalized absorption and emission spectra of **3a–d** in acetonitrile at room temperature, and Table 1 summarizes the photophysical data. Comparing the absorption spectra of the new ligands **3** to that of the parent 1,10-phenanthroline shows a substantial red-shift of the major electronic transitions.[11] Upon excitation at 342 nm, the unsubstituted derivative **3a** exhibits an intense purple emission that tails into the visible and displays maxima at 375 and 392 nm. Although only modestly red-shifted when compared to the emission of the parent 1,10-phenathroline, a substantial increase in fluorescence quantum yield is observed ($\phi_F = 0.41$). An additional bathochromic shift is obtained by substituting electron-donating groups into the conjugated

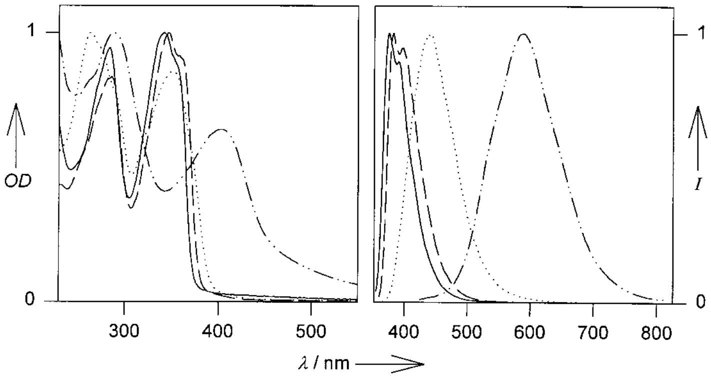


Figure 1. Normalized absorption and emission spectra of **3a** (——), **3b**(–––), **3c** (••••), and **3d** (•–•–) in acetonitrile. Emission spectra were obtained upon excitation at the absorption maximum.

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Table 1. Photophysical data for conjugated phenanthrolines **3**.

Compd.	λ_{max} [nm][a]	λ_{em} [nm][b]	$\lambda_{max}(Zn^{2+})$ [nm][c]	$\lambda_{em}(Zn^{2+})$ [nm][d]	$\lambda_{max}(H^+)$ [nm][e]	$\lambda_{em}(H^+)$ [nm][f]	ϕ_F[g]	τ [ns][h]
3a	342 (346)	375, 392 (376, 395)	372 (384)	434 (415)	394 (394)	490 (472)	0.41 (0.49)	2.93
3b	346 (350)	383, 396 (384, 404)	374 (394)	453 (436)	398 (414)	525 (514)	1.0 (0.73)	1.50
3c	350 (358)	441 (416)	382 (392)	530[i] (490)	378 (418)	532[i] (489)	0.64 (0.87)	1.71
3d	402 (410)	587 (523)	454 (474)	–[j] (646)[i]	352 (368)	408 (398, 417)	–[k]	–[k]

[a] Absorption maxima in acetonitrile and dichloromethane (in parenthesis), ±2 nm. [b] Emission maxima in acetonitrile and dichloromethane (in parenthesis), ±2 nm. Emission wavelengths are not corrected for instrument response. Correction gives a slight red-shift (6–10 nm) for the emission maxima of **3c** and **3d**. [c] Absorption maxima in acetonitrile and dichloromethane (in parenthesis) in the presence of excess $ZnCl_2$, ±2 nm. [d] Emission maxima in acetonitrile and dichloromethane (in parenthesis) in the presence of excess $ZnCl_2$, ±2 nm. [e] Absorption maxima in acetonitrile and dichloromethane (in parenthesis) in the presence of excess CH_3SO_3H, ±2 nm. [f] Emission maxima in acetonitrile and dichloromethane (in parenthesis) in the presence of excess CH_3SO_3H, ±2 nm. [g] Fluorescence quantum yield in acetonitrile and dichloromethane (in parenthesis) determined relative to 9,10-diphenylanthracene (see Experimental Section). [h] Excited-state lifetime, ±0.02 ns. [i] Weak emission. [j] Quenched emission. [k] Not determined; see ref. [12].

phenyl rings. Thus, the tolyl derivative **3b** emits at 383 and 396 nm with an excellent fluorescent quantum efficiency ($\phi_F = 1.0$). Exciting a dilute solution of the 4-methoxyphenyl derivative **3c** in acetonitrile results in a bright blue emission, well within the visible range ($\lambda_{em} = 441$ nm, $\phi_F = 0.64$). A remarkable red-shift of the emission is observed with the *N,N*-dimethylamino derivative **3d.** In acetonitrile, a broad emission centered around $\lambda_{em} = 587$ nm gives rise to an orange emission.[12] Extending the 1,10-phenanthroline skeleton with arylethynyl groups thus shifts the emission into the visible region and results in considerable increase in fluorescence quantum efficiency with certain ligands approaching unity.[13]

Solvent polarity has little influence on the absorption maxima of the conjugated ligands and a profound effect on their emission behavior. As illustrated in Figure 2, the parent derivative **3a** is rather insensitive to solvent composition, while the emission maximum of the anisyl derivative **3c** is much more susceptible to solvent polarity. The red-shift observed for **3c** upon increasing solvent polarity is indicative of greater stabilization of the excited state. This trend occurs in polar molecules that are likely to have enlarged dipoles and charge-transfer character in their excited state.[14] Importantly, the weak emission of 1,10-phenanthroline is blue-shifted upon increasing solvent polarity.[6] This behavior was attributed to a close proximity of the π–π* and *n*–π* singlet excited states, with the latter becoming more contributing in nonpolar solvents.[6] This may explain the low fluorescence quantum efficiency of 1,10-phenanthroline, since *n*–π* excited states often decay by nonradiative pathways. In contrast, the conjugated phenanthroline ligands **3** exhibit high fluorescence quantum efficiencies in various solvents and short excited-state lifetimes (1.5–3 ns, Table 1), suggesting that the emitting excited state is a singlet π–π* state.[15]

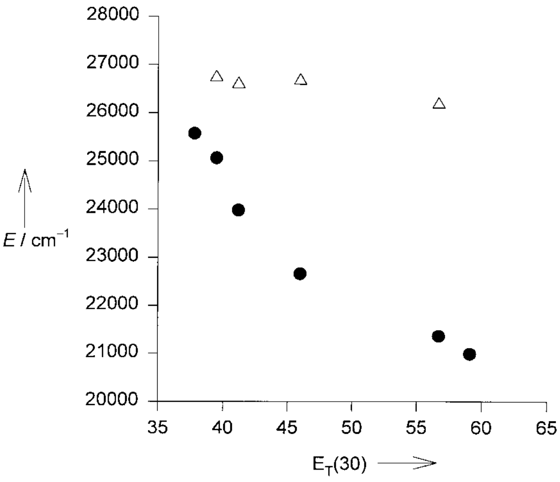

Figure 2. Solvent-dependent emission energies for **3a** (△) and **3c** (●) (see Experimental Section).

Further modulation of emission wavelengths is attained by the addition of exogenous ions. Upon titrating Zn^{2+} ions into a solution of the phenylethynyl derivative **3a** in acetonitrile, the emission color dramatically changes from purple to bright blue (Table 1). Similarly, a shift of approximately 70 nm is observed upon addition of Zn^{2+} ions to the tolyl derivative **3b** yielding an intense blue emission. A bright yellow fluorescence, centered at 530 nm, is observed when Zn^{2+} ions are added to a solution of the 4-methoxyphenylethynyl derivative **3c** in acetonitrile. More profound shifts are observed when strong acids are added to protonate the conjugated ligands. While the parent derivative **3a** exhibits a bright purple emission centered slightly below 400 nm, addition of methanesulfonic acid to its solution in acetonitrile causes a bathochromic shift of approximately 100 nm, and an intense yellow-green emission centered at 490 nm is observed.[16] A slightly smaller shift to longer wavelengths is observed in dichloromethane, as expected for a less polar solvent (Table 1). Importantly, a relatively small drop in fluorescence quantum efficiency is observed upon protonation ($\phi_F = 0.33$ for **3a**·H^+ in CH_2Cl_2). Figure 3 illustrates the dramatic spectral changes ligand **3b** undergoes upon the addition of exogenous ions.[17]

Fluorescent compounds have been attracting considerable interest in recent years as components for fluorescent sensors and switches.[18–22] Yet, highly emissive tunable chromophores are rare.[23, 24] The combination of a highly coordinating diimine functionality and an extended conjugation through ethynyl linkages provides a unique family of tunable intrinsic fluorophores, where changes in the electronic polarization, solvation, and coordination are translated into dramatic spectral changes. The simple synthesis, together with the availability of numerous precursors and cross-coupling methodologies, make the preparation of other 1,10-phenanthroline-based chromophores with diverse absorption and emission characteristics almost trivial. The visible emission of the conjugated ligands and their complexes, as well as their

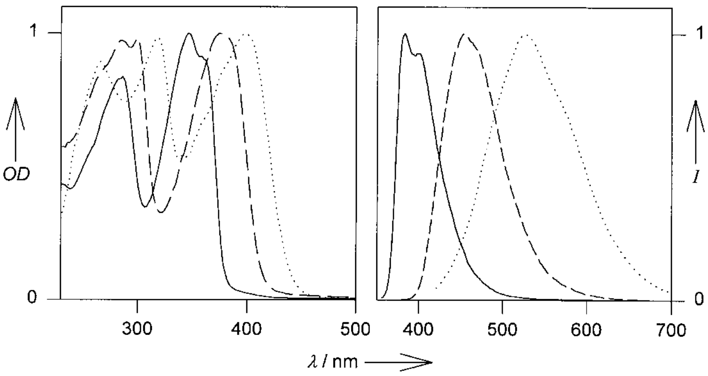

Figure 3. Normalized absorption and emission spectra of **3b** (——), **3b** + excess Zn^{2+} (– – –), and **3b** + excess methanesulfonic acid (••••) in acetonitrile. Emission spectra were obtained upon excitation at the absorption maximum.

relatively long excitation wavelengths (> 340 nm), may facilitate the incorporation of these chromophores into biologically useful chemosensors as well as novel light-emitting materials.

Experimental Section

The synthesis of 3,8-dibromo-1,10-phenanthroline[9, 10] and 3,8-bis(arylethynyl)-1,10-phenanthrolines[11] has been previously reported. Representative data for **3b**: m.p. 243 °C; MS: m/z 408 [M^+]; IR (KBr): $\tilde{\nu}$ 2210 cm^{-1} (C≡C); UV (CH_3CN): λ_{max} ($\varepsilon \times 10^{-4}$) = 286 (5.1), 346 (6.1), 362 nm (5.4); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.28 (d, J = 2.2 Hz, 2H, phen H2/9), 8.37 (d, J = 2.2 Hz, 2H, phen H4/7), 7.80 (s, 2H, phen H5/6), 7.52 (d, J = 8 Hz, 4H, ph), 7.22 (d, J = 8 Hz, 4H, ph), 2.41 (s, 6H, CH_3).

Fluorescence quantum yields (ϕ_F) were measured by using a Perkin Elmer LS50B Luminescence Spectrometer with optically thin solutions (OD = 0.04) at room temperature. Argon-degassed, isoabsorptive solutions of the standard and conjugated phenanthroline derivatives **3a–d** were excited at the wavelength of maximum absorption of the ligands. Values are reported relative to 9,10-diphenylanthracene and calculated according to Equation (1),[25] where ϕ_{unk} is the fluorescence quantum yield of the sample, ϕ_{std} is the quantum yield of the standard (ϕ_F = 0.91 in ethanol),[26] I_{unk} and I_{std} are the integrated emission intensities of the sample and the standard, respectively, A_{unk} and A_{std} are the absorbances of the sample and the standard at the excitation wavelength, respectively, and η_{unk} and η_{std} are the refractive indexes of the corresponding solutions (pure solvents were assumed).

$$\phi_{unk} = \phi_{std}\left(\frac{I_{unk}}{A_{unk}}\right)\left(\frac{A_{std}}{I_{std}}\right)\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2 \qquad (1)$$

Multiple measurements indicated a precision of about 5% for the ϕ_F values determined. The fluorescence quantum yields were qualitatively confirmed by calculating $\phi_F = \tau_s/\tau_0$ (where τ_0 is the "native" lifetime and τ_s is the experimentally determined one). The native lifetime is obtained by integrating the absorption band and determining the oscillator strength.[27, 28]

The dependence of emission energies on solvent polarity was determined in dichloromethane/cyclohexane mixtures (low polarity), and acetonitrile/water mixtures (high polarity). Emission spectra were converted from wavelength (nm) to frequency (cm^{-1}) units. $E_T(30)$ values were experimentally determined for each solvent mixture using Reichardt's salt.[29]

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Synthesis of Giant Zeolite Crystals by a Bulk-Material Dissolution Technique**

Shinichi Shimizu* and Hideaki Hamada

Zeolites are crystalline microporous materials that are attracting much attention owing to their applications as high-performance catalysts, in separation processes, and in optical, magnetic, and electronic devices.[1] Major efforts have been undertaken to synthesize large single crystals with a well-defined habit, because some applications require large zeolite crystals to allow effective use of their micropores. In 1971 Charnell synthesized zeolite Na-A (LTA) crystals (ca. 65μm) and zeolite Na-X (FAU) crystals (ca. 140 μm) under hydrothermal conditions from gels of sodium metasilicate, sodium aluminate, and triethanolamine, which were purified to remove particles by a precision filtration technique.[2] In 1993 a novel method to synthesize zeolites in nonaqueous media was developed to obtain giant zeolite crystals by controlling the release and solubility of reactive solution species in organothermal systems.[3] Giant crystals of dodecasil-3C, a clathrasil having the MTN framework, were prepared by using a combination of silica rods and fumed silica by Klemperer and Marquart.[4] Other attempts to obtain large zeolite crystals have also been made.[5]

Recently, we developed a novel technique for synthesizing giant zeolite crystals in aqueous media by controlling the solubility in hydrothermal systems. Both silicalite-1 (all-silica MFI) and analcime (ANA) crystals with sizes of about 3 mm, which were unknown until now, were successfully synthesized by using bulk materials as the silica and alumina sources (bulk-material dissolution (BMD) technique). The compositions of the reaction mixtures and the experimental results are summarized in Table 1. A typical procedure is as follows: A piece of quartz glass tube (ca. 24 mm long, 10 mm external and 8 mm internal diameter; 25.2 mmol SiO_2) was placed in a PTFE sleeve (capacity 23 mL) equipped for an autoclave. The sleeve was filled with an aqueous solution containing tetra-*n*-propylammonium hydroxide (TPAOH) and hydrogen fluoride (HF). The experimental setup is illustrated in Figure 1.

Table 1. Synthesis of zeolite crystals by the BMD technique.

Zeolite framework (Figure)	Bulk source [mmol]	Liquid phase [mmol]	T [°C]	t [d]	Maximum crystal size [μm]
MFI (2, 3)	SiO_2 tube SiO_2 (25.2)	TPAOH (8.9) HF (9.7) H_2O (870)	200	25	2000 × 1000 × 1000
MFI (4)	SiO_2 tube SiO_2 (18.4)	TPAOH (8.9) HF (14.6) H_2O (885)	200	46	3200 × 2800 × 2600
ANA (5)	ceramic boat SiO_2 (12.1) Al_2O_3 (3.0)	NaOH (20.3) H_2O (847)	200	31	3000 × 2800 × 2500
JBW & CAN (6)	ceramic tube SiO_2 (12.6) Al_2O_3 (9.6)	NaOH (51.2) H_2O (683)	200	7	640 × 320 × 100 (JBW) 300 × 5 × 5 (CAN)
CAN	ceramic boat SiO_2 (11.4) Al_2O_3 (2.8)	NaOH (99.0) H_2O (832)	200	13	100 × 20 × 20
SOD	ceramic boat SiO_2 (11.0) Al_2O_3 (2.7)	NaOH (51.0) H_2O (833)	100	19	60 × 60 × 60
SOD	ceramic tube SiO_2 (21.7) Al_2O_3 (11.7)	NaOH (98.7) H_2O (697)	200	12	120 × 120 × 120

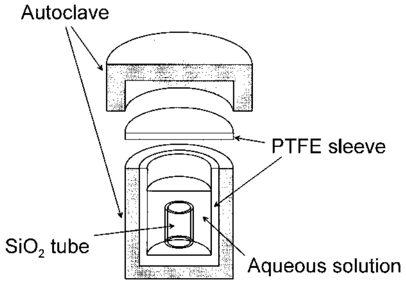

Figure 1. Schematic illustration of the experimental setup for BMD crystallization.

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