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Efficient Synthesis and Characterization of Novel Bibenzimidazole Oligomers and Polymers as Potential Conjugated Chelating Ligands

Jun Yin and Ronald L. Elsenbaumer*

Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019

elsenbaumer@uta.edu

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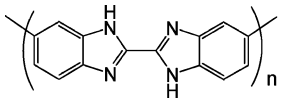

n = 1, 2, 3, 4, ..., n.

A simple and mild condensation route for the synthesis of novel bibenzimidazole oligomers and polymers is reported here using methyl 2,2,2-trichloroacetimidate as a key starting material. The dimer, trimer, tetramer, and polymers of bibenzimidazole were synthesized as a new series of potential conjugated chelating ligands for metallopolymer studies. The polymers show a maximum absorption at around 400 nm. The optical band gap of the polymer was estimated to be 2.68 eV.

Introduction

Metal-complexed conjugated polymers have attracted significant attention in recent years.[1−4] A variety of π-conjugated heteroaromatic polymers which serve as electrically conducting, rigid chelating ligands have been prepared, and their metal complexes have been investigated.[5−7] They offer much promise in the development of nanoelectronics, electrocatalysts, sensors, and optical devices.

It has been demonstrated by Pickup and co-workers that the existence of superexchange interactions between metal centers coordinated to conjugated polymer backbones enhanced the rate of electron transport through the polymer in a series of Ru- and Os-complexed polybenzimidazoles based on benzimidazole-pyridine or benzimidazole-pyrazine as the repeat units.[7−9] It was predicted that higher rates of electron transport could be achieved by better matching of orbital energies between the metal-based dπ orbitals and the polymer π or π^* orbitals.

To probe the orbital interactions between metals and conjugated polymers, poly(bibenzimidazoles) with 2,2′-bibenzimidazole (**1**) as the repeat unit were chosen in our research as the π-conjugated backbones. It appears that polybenzimidazoles are attractive choices for a number of reasons.[4] They tend to be very robust and remain stable under considerable thermal and chemical stress.[10] The studies of binuclear benzimidazole complexes have shown that they possess significant electronic coupling between two metals.[11−13] In addition, removal of the imidazole proton allows pH control of the electron density on the conjugated ligands.[14−21]

* To whom correspondence should be addressed. Phone: 1-817-272-1021. Fax: 1-817-272-2625.

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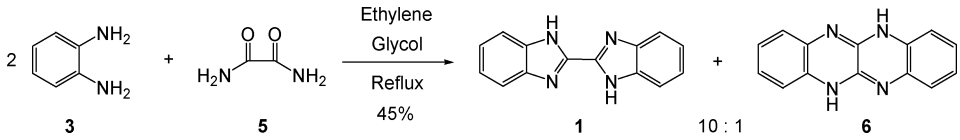
SCHEME 1. Formation of 2,2′-Bibenzimidazole and Byproduct



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Polybenzimidazoles are generally synthesized via melt polymerization of aromatic bis(*o*-diamine)s with aromatic dicarboxylic acid derivatives.[22−24] Another common method is solution polymerization performed in poly(phosphoric acid).[25] However, the drawbacks with these protocols often include high temperatures, long reaction times, and strongly acidic conditions. In addition, the structures and the molecular weights of the obtained polymers are difficult to determine. Our initial attempts using these methods for the synthesis of poly(bibenzimidazole) met with limited success when using them for further metal complexation.

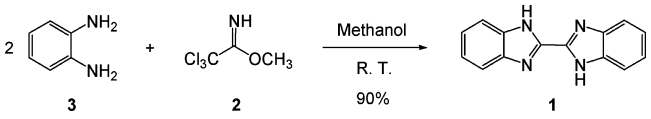
In this regard, the synthesis and investigation of a discrete set of oligomers with precise lengths has been an exciting approach to provide specific information for interpreting structural and conformational properties of the corresponding polymers.[26] This is because oligomers serve as excellent models for the solution, electronic, photonic, thermal, and morphological properties of their corresponding polymers.[26] In addition, the metal complexes of the oligomers would also provide further information about the metallopolymers. However, the synthesis of well-defined bibenzimidazole oligomers has not been reported.

In this paper, we report a concise and mild route for the first synthesis of bibenzimidazole oligomers using methyl 2,2,2-trichloroacetimidate (**2**) as the key starting material. From a retrosynthetic standpoint, a bibenzimidazole unit is constructed via a ring-closure reaction of *o*-phenylenediamine (**3**) with 2-trichloromethylbenzimidazole (**4**) or its derivative. This methodology does not involve tedious precursor synthesis and metal-catalyzed aryl−aryl bond formation, which is commonly used for heterocyclic aromatic oligomer and polymer synthesis.[27]

Results and Discussion

Synthesis of Bibenzimidazole Monomer. Initial attempts for the synthesis of 2,2′-bibenzimidazole monomer (**1**) followed the most commonly used method in the literature via a condensation reaction of *o*-phenylenediamine (**3**) and oxamide (**5**) in ethylene glycol at reflux, which was reported by Fieselmann et al. in 1978 (Scheme 1).[28] However, the drawbacks of this approach are the high reaction temperature (around 196 °C), low product yield, and difficulties in the purification of the desired product due to the formation of an isomeric byproduct **6** (ca. 10%).[29] Interestingly, the formation of **6** in this reaction was never reported in the literature. Due to the similar solubility as that of 2,2′-bibenzimidazole, the byproduct **6** was very difficult to separate from the desired monomer. Furthermore, this method cannot be extended to the synthesis of either bibenzimidazole oligomers or polymers due to the nature of the reaction and the formation of the mixed products.

SCHEME 2. Holan's Synthesis of 2,2′-Bibenzimidazole



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Therefore, an alternative and more efficient approach was required. In an older report, in 1967, Holan and coworkers published a series of papers describing their excellent studies on the synthesis and reactions of 2-trichloromethylbenzimidazole (**4**).[30−33] A mild and efficient synthesis of 2,2′-bibenzimidazole (**1**) was also reported by simply reacting *o*-phenylenediamine (**3**) with methyl 2,2,2-trichloroacetimidate (**2**) in methanol at room temperature (Scheme 2). The pure product **1** was obtained in an excellent 90% yield after a simple filtration. The advantages of this method are obvious: the reaction occurred at room temperature; the desired product precipitated out from the reaction mixture, which allowed easy separation and purification; no byproduct formed; and recrystallization was not necessary. Surprisingly, despite the practical convenience, high yields, simple product purification, and mild reaction conditions, this approach for the synthesis of bibenzimidazole has been overlooked in the literature.

Intrigued by these advantages, we explored the synthesis of bibenzimidazole oligomers by utilizing similar methodology for the construction of the bibenzimidazole unit. The successful extension of this efficient method for the synthesis of bibenzimidazole oligomers ($n = 2-4$, n is the number of the repeat units in the oligomers) and the applications for the synthesis of bibenzimidazole polymers are described in this paper.

Synthesis of Bibenzimidazole Dimer. Following Holan's procedures,[30] the key intermediate 2-trichloromethylbenzimidazole (**4**) for the synthesis of the oligomers was prepared by reacting *o*-phenylenediamine (**3**) with methyl 2,2,2-trichloroacetimidate (**2**) in acetic acid. The use of a weak acid, e.g., acetic acid, was the key to

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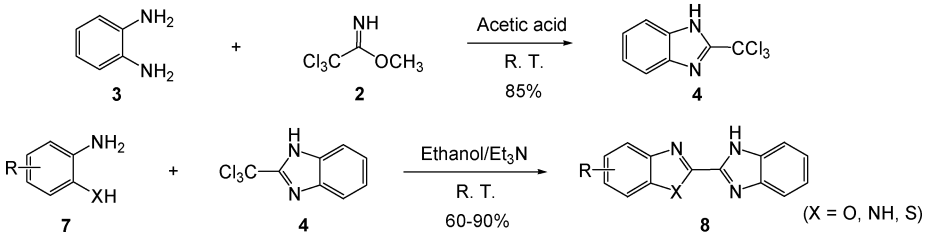
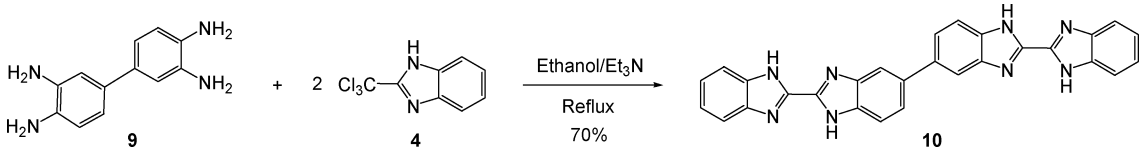
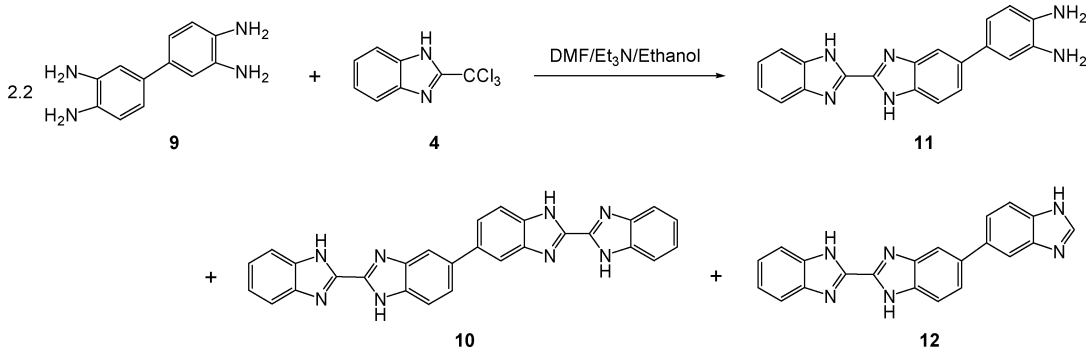
SCHEME 3. Holan's Synthesis and Reactions of Trichloride 4



SCHEME 4. Synthesis of Bibenzimidazole Dimer 10



SCHEME 5. Synthesis of 4-Bibenzimidazole-Substituted *o*-Phenylenediamine 11



the successful suppression of the formation of bibenzimidazole (**1**) and isolation of the relatively stable trichloride **4**. Holan and co-workers have demonstrated that **4** can react with a variety of *o*-bifunctional nucleophiles **7** to generate heterocyclic ring systems **8** (Scheme 3).[33]

We have found that when 3,3′-diaminobenzidine (**9**) was employed as a bis-*o*-bifunctional nucleophile and treated with two equiv of trichloride **4** under similar reaction conditions at reflux, the desired bibenzimidazole dimer **10** was obtained in 70% yield (Scheme 4).

The X-ray structure determination reveals that it is a rigid coplanar structure, and this will be discussed in detail below (Figure 2).

Synthesis of Diamino Compound 11. The key nonsymmetric building block for the synthesis of bibenzimidazole trimer and the tetramer is the 4-bibenzimidazole-substituted *o*-phenylenediamine derivative **11** (Scheme 5). It possesses one bibenzimidazole unit with an *o*-phenylenediamino functionality, which could further participate in a similar cyclization process with either imidate **2** or trichloride **4** as *o*-phenylenediamine (**3**) does (Schemes 2 and 3) to generate more bibenzimidazole units.

To synthesize compound **11**, the cyclization of 3,3′-diaminobenzidine **9** with trichloride **4** has to occur on one side of 3,3′-diaminobenzidine, which could be achieved by controlling the stoichiometry. Therefore, when trichloride **4** was treated with an excess of 3,3′-diaminobenzidine in DMF at room temperature for several hours and then heated at 130 °C for 44 h, the desired amine **11** was obtained in 51% yield, along with 6% of the dimer **10**. A third byproduct was also isolated in 30% yield (entry 1, Table 1), for which ^{1}H NMR spectroscopy showed a singlet proton at 9.25 ppm. In accordance with the spectroscopy data, the structure of the byproduct was assigned as **12**, presumably produced by the cyclization of the diamine **11** with DMF.

TABLE 1. Comparison of the Reactions that Occurred at Different Temperatures in Scheme 5

entry	reaction conditions	diamine **11** (%)	dimer **10** (%)	byproduct **12** (%)
1	RT 5 h, then 130 °C 44 h	51	6	30
2	RT 5 h, then 75 °C 7−10 h	63	10	0

Subsequent control experiments provided supportive evidence for the formation of byproduct **12**. For example, when diamine **11** was heated in DMF in the presence or absence of Et_3N, **12** was formed exclusively in ca. 76% yield. It is interesting to note that the formation of benzimidazole derivative by the cyclization of aromatic diamine with DMF without an appropriate activating agent has not been reported in the literature.[34]

To prevent the further cyclization of diamine **11** with DMF, the reaction of trichloride **4** with 3,3′-diaminobenzidine (**9**) was performed at a relatively low temperature: room temperature for several hours, then at 75−80 °C for 7−10 h. Under these conditions, the formation of byproduct **12** was completely suppressed and the desired diamine **11** was obtained in a satisfactory 63% yield, along with a small amount of the dimer **10** (ca.

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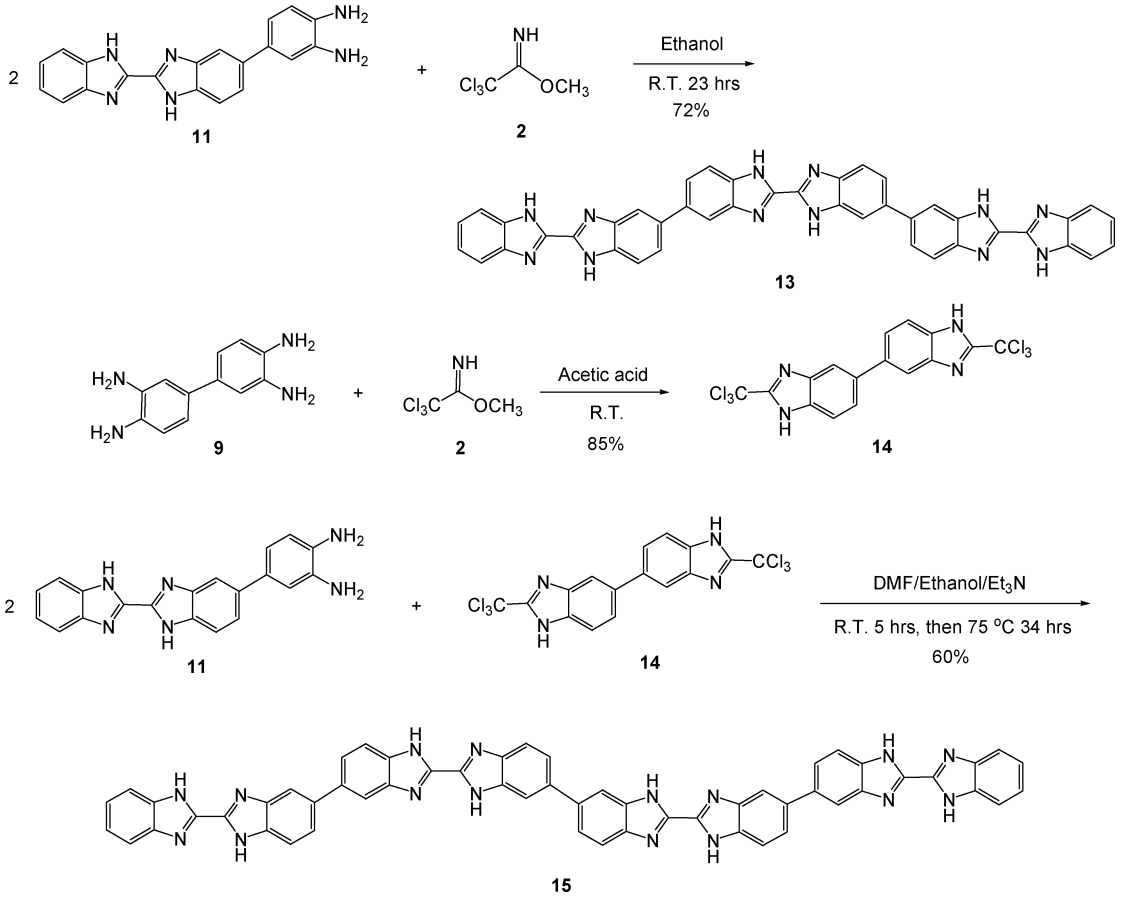
SCHEME 6. Synthesis of Bibenzimidazole Trimer 13 and Tetramer 15



10%) (entry 2, Table 1), which was readily separated from **11** by fractional precipitation.

Synthesis of Bibenzimidazole Trimer and Tetramer. With **11** in hand, the synthesis of the trimer **13** was readily achieved by condensation of two equiv of **11** with imidate **2** at room temperature in 72% yield, following the same strategy used for the synthesis of 2,2′-bibenzimidazole (**1**) from *o*-phenylenediamine (Scheme 6).

Another important symmetric difunctional building block for the synthesis of the tetramer, bis(trichloride) (**14**), was synthesized using the same strategy as that used for 2-trichloromethylbenzimidazole (**4**). 3,3′-Diaminobenzidine (**9**) was treated with 2.2 equiv of imidate **2** in acetic acid to provide the desired bis(trichloride) **14**, which precipitated out from the reaction medium and was isolated in an excellent 85% yield after a simple filtration.

With both diamine **11** and bis(trichloride) **14** accessible, the tetramer **15** was synthesized by condensation of two equiv of **11** with one equiv of **14** using the previous diamine trichloride cyclization conditions (Scheme 6). The product **15** precipitated from the reaction medium and was isolated in 60% yield. A small amount of DMF cyclization byproduct **12** was also formed under the reaction conditions and was removed by trituration of the crude product in DMF under heating (around 130 °C).

The melting point of the monomer bibenzimidazole **1** was greater than 300 °C.[29] The melting points of the oligomers (**10**, **13**, **15**) were not measured due to the high temperature. The thermal properties of polybenzimidazoles have been widely investigated.[10] The polybenzimidazoles have T_g's greater than 430 °C.[10] The thermal properties are discussed in the following section.

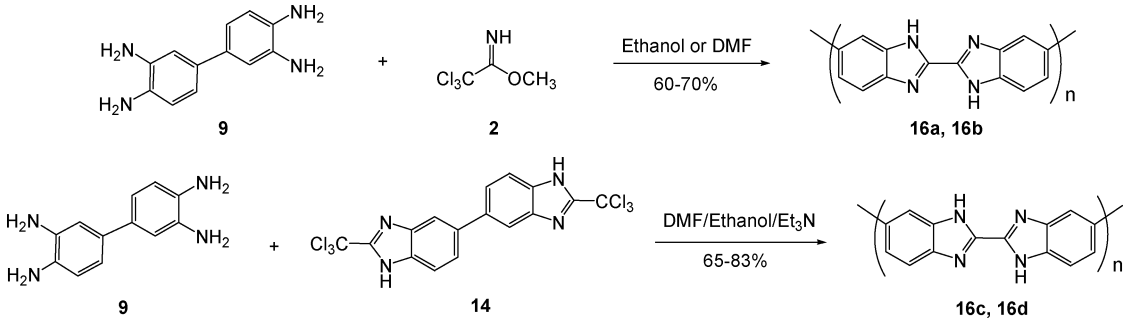
The dimer, trimer, and tetramer are all brownish yellow powders and are soluble in concentrated sulfuric acid and methanesulfonic acid. The dimer is soluble in DMAC, DMF, DMSO, CF_3COOH, and HCOOH. The trimer and tetramer are partially soluble in DMAC and HCOOH and sparingly soluble in DMF, DMSO, NMP, and CF_3COOH.

Synthesis of Bibenzimidazole Polymer. Poly(bibenzimidazoles) were synthesized by two methods (Scheme 7). One method is the polycondensation reaction between diaminobenzidine **9** and acetimidate **2** in different solvents. For polymer **16a**, the interfacial polycondensation of equal amounts of 3,3′-diaminobenzidine (**9**) and methyl 2,2,2-trichloroacetimidate (**2**) was carried out in a nonsolvent ethanol. The reaction was initiated at room temperature and then heated to reflux for 82 h to ensure that the cyclization went to completion. The brown polymer **16a** was obtained by simple filtration in 70% yield. The number average molecular weight (M_n) was around 19 000 based on the viscosity determination (discussed in the viscosity section).

The synthesis of polymer **16b** was carried out in a homogeneous solution using DMF as the solvent in the presence of ethanol. The brown polymer **16b** precipitated out from the solution in 60% yield with a number average molecular weight (M_n) around 15 000.

The comparison of these two reaction conditions indicates that the interfacial polymerization gave a higher

SCHEME 7. Synthesis of Poly(bibenzimidazole) 16a−d[a]



[a] **16a**: In ethanol, RT, then reflux. **16b**: In DMF in the presence of ethanol, RT, then 75 °C. **16c**: RT, then 75−80 °C. **16d**: RT, then 75 °C, then 120−130 °C, and then 150 °C.

molecular weight polymer (**16a**) than the solution polymerization, which produces polymer **16b**. On the basis of Holan's study of the reaction between the diamino compound and methyl 2,2,2-trichloroacetimidate (**2**),[30] the reactions need to be initiated at room temperature for at least several hours and then heated to around 70 °C to ensure that the cyclization goes to completion. If the reaction is heated directly to 70 °C without being stirred at room temperature, it would not provide the polymer with the expected structure.

The other method of synthesizing poly(bibenzimidazole) (**16c**−**d**) is the polycondensation reaction between diaminobenzidine **9** and bis(trichloride) **14** in DMF under different conditions. The direct polycondensation of equal amounts of 3,3′-diaminobenzidine (**9**) and bis(trichloride) **14** was carried out in a homogeneous DMF solution in the presence of Et_3N and ethanol. For polymer **16c**, the reaction was initiated at room temperature for 5 h, then heated to 75 °C, and kept at 75−80 °C for 72 h. The orange-colored polymer was obtained by addition of water to the reaction mixture and precipitated out in 83% yield.

For polymer **16d**, the reaction was initiated at room temperature for 5 h, then heated to 75 °C, then to 120−130 °C, and eventually to a maximum of 150 °C. The greenish yellow polymer **16d** precipitated out from the reaction mixture and was isolated in 65% yield.

Polymer **16c** has a higher molecular weight (M_n = 9600) than does polymer **16d** (M_n = 6400). Keeping the reaction temperature at 75 °C leads to the formation of the higher molecular weight polymer **16c**. For polymer **16d**, the temperature was eventually increased to 150 °C, which might lead to the cyclization of the diamino groups with DMF and therefore terminate the chain growth.

Polymers **16a**,**b** are partially soluble in concentrated sulfuric acid, methanesulfonic acid, and HCOOH but are not soluble in CF_3COOH, DMAC, DMF, DMSO, and NMP. Polymer **16c** is soluble in all the above solvents. Polymer **16d** is soluble in concentrated sulfuric acid and methanesulfonic acid; partially soluble in HCOOH and CF_3COOH; not soluble in DMAC, DMF, DMSO, and NMP. The solubility of polymer **16c** is different from those of polymers **16a**,**b**, and **d**, probably because the reaction temperature of 75 °C is not high enough for the complete cyclization in the polymer chains.

NMR Studies of the Oligomers. ^1H NMR spectra of the oligomers (**1**, **10**, **13**, and **15**) are shown in Figure 1. To clarify the NMR spectra by removing the tautomer effect,[35] CF_3COOD was used as the solvent, as well as forming the trifluoroacetate salts of the oligomers. The crystal structure of dimer **10** shows that the rings are coplanar and the molecule is centrosymmetric. In the aromatic region of the ^1H NMR spectrum, the dimer shows five groups of peaks (H_1, H_2, H_3, $H_{4/4'}$, and $H_{5/5'}$). The singlet (H_1) is at 8.43 ppm; there are two double doublets at 8.28 and 8.26 ppm, which represent the protons H_2 and H_3 in the repeat unit; there are two double doublets at 8.12 and 7.93 ppm, which represent the protons $H_{4/4'}$ and $H_{5/5'}$ on both sides of the end groups. The NMR spectrum of trimer **13** and dimer **10** are very similar, which indicates that the trimer might have the coplanar structure. But the spectrum of the tetramer **15** is a little different from those of the dimer and the trimer. There are three singlets representing H_1, $H_{1'}$, and $H_{1''}$, respectively, instead of one singlet in the dimer and trimer; $H_{2/2'/2''}$ and $H_{3/3'/3''}$ show multiplets instead of the two double doublets in the dimer and the trimer. This indicates that H_1, $H_{1'}$, $H_{1''}$ are different, as well as H_2, $H_{2'}$, $H_{2''}$ and H_3, $H_{3'}$, $H_{3''}$. The tetramer may not have the coplanar structure that the dimer does. This noncentrosymmetric nature may lead to the nonequivalence of the protons in the repeat units.

X-ray Structure of the Dimer. Yellow block single crystals of the CF_3COOH salt of dimer **10** were grown by slow evaporation of a CF_3COOH solution at room temperature [monoclinic space group $P2_1/C$ (Figure 2)]. The X-ray crystal structure analysis reveals the almost coplanar structure of the dimer. One dimer of bibenzimidazole was protonated with four CF_3COOH molecules, and the rest of the CF_3COOH molecules are in the lattice to support the crystals by intermolecular H-bonding interactions. The protonated bis(bibenzimidazole) formed a zigzag pattern with alternating stacking columns. The structure indicates an efficient π-stacking in the solid state with an intermolecular spacing of 7.90 Å.

UV−vis Properties. The UV−vis properties of the oligomers and the polymers were investigated in the protonated forms in methanesulfonic acid (Figures 3−6, Table 2). The bibenzimidazole monomer **1** has a maximum absorption at 340 nm, which represents the $\pi-\pi^*$ transition. The X-ray crystal analysis of dimer **10** shows the coplanar structure. Its λ_{max} ($\pi-\pi^*$ transition) is at 373 nm, which indicates the extension of the conjugation.

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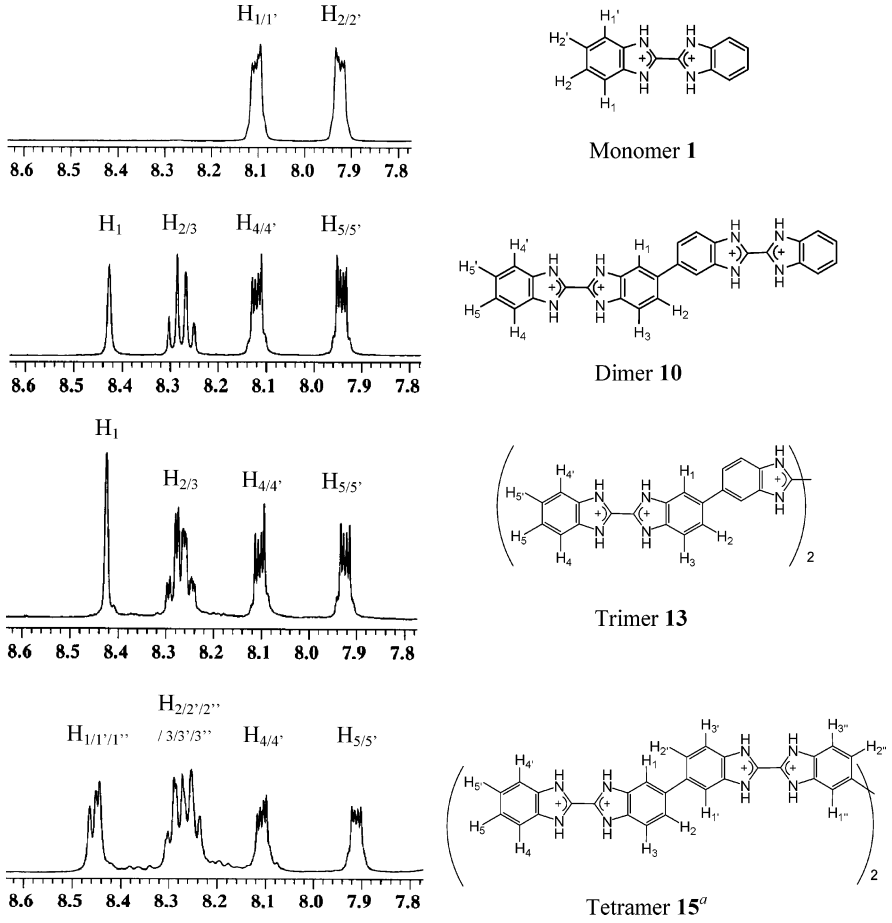

FIGURE 1. NMR spectra of the oligomers in CF_3COOD; the CF_3COO^- counterions were omitted from the structures for clarity; "*a*" indicates that the NMR of the tetramer was in CF_3COOD/D_2O to improve the solubility.

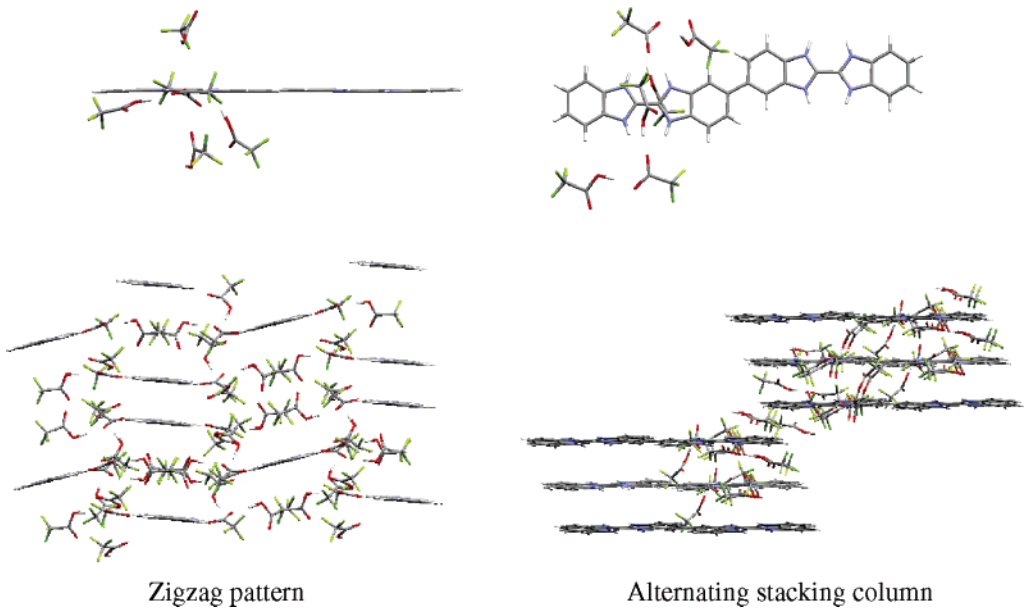

FIGURE 2. Crystal structure and packing pattern of $[bis(bibenzimidazole)]_2(CF_3COOH)_{12}$.

The λ_{max} of the trimer **13** is at 382 nm, which indicates further extension of conjugation, but not as much as from the monomer to the dimer. The tetramer **15** only red-shifted 7 nm to 389 nm compared to that of the trimer, which indicates the large chain length extension does not produce the expected further decrease of the HOMO−LUMO gap. This phenomenon indicates that the structure of the tetramer might not be coplanar.

Figure 4 shows the linear relationship between the extinction coefficient and the number of the repeat unit

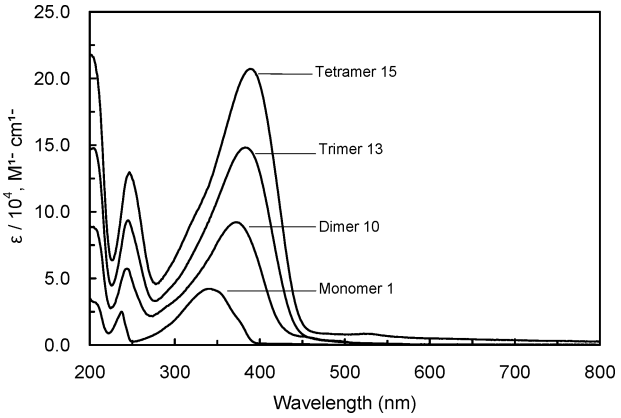

FIGURE 3. UV−vis spectra of the oligomers in methanesulfonic acid (10^{-6} M).

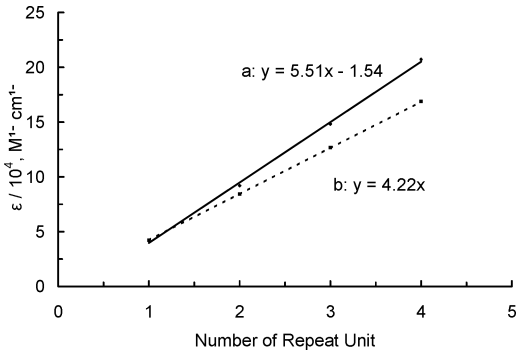

FIGURE 4. Extinction coefficient vs the number of repeat unit in the oligomers. (a, solid line): Experimental value; there are interactions between the repeat units due to the π orbital overlap. (b, dotted line): Theoretical values, assuming the repeat units are isolated with no interactions.

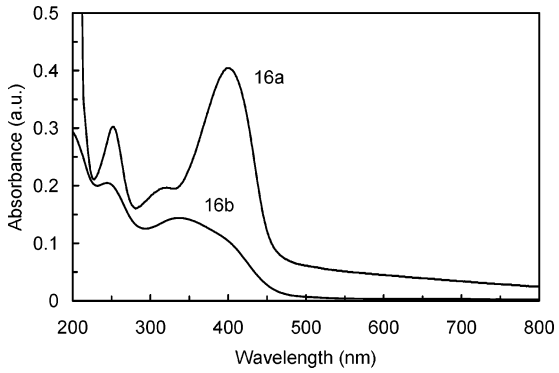

FIGURE 5. UV−vis spectra of the polymers **16a,b** in methanesulfonic acid (10^{-6} M).

in the oligomers. The solid line, a, is the experimental data; the dotted line, b, is the theoretical data assuming that there is no interaction between the repeat units. The slope of the solid line a (5.51×10^4) is larger than that of the dotted line b (4.22×10^4), which indicates that there are some interactions between the repeat units due to the π orbital overlap. The extinction coefficients ϵ ($M^{-1}\cdot cm^{-1}$) per repeat unit were found to be 4.22×10^4 in the monomer, 4.61×10^4 in the dimer, 4.94×10^4 in the trimer, and 5.18×10^4 in the tetramer. This suggests that in the tetramer, one repeat unit absorbs 1.2 times more light than one repeat unit in the monomer. The

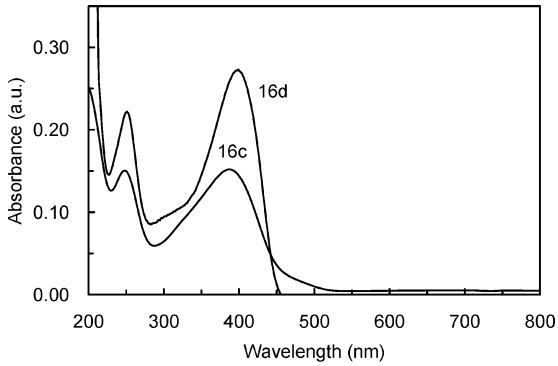

FIGURE 6. UV−vis spectra of the polymers **16c,d** in methanesulfonic acid (10^{-6} M).

TABLE 2. Photophysical Properties of Bibenzimidazole Oligomers and Polymers

compound	MW	λ_{max}^{abs} (nm)	ϵ (10^4, $M^{-1}\cdot cm^{-1}$)	E_g (eV)	λ_{max}^{em} (nm)	Stokes shift (nm)
monomer **1**	234.28	340	4.22		414	74
dimer **10**	466.54	373	9.21	2.89	495	122
trimer **13**	698.74	382	14.82	2.81	495	113
tetramer **15**	930.98	389	20.72	2.78	490	101
polymer **16a**	19000	400		2.68	498	98
polymer **16b**	15000	400		2.65	495	95
polymer **16c**	9600	388		2.70	505	117
polymer **16d**	6400	397		2.75	495	98

extinction coefficients of the trimer and the tetramer are larger than 140 000 $M^{-1}\cdot cm^{-1}$, which is unusually large for the short chain oligomers.

The λ_{max} values of the polymers **16a**−**d** were at 388−400 nm, which were very similar to that of the tetramer (Figures 5 and 6). From the onset of the absorptions, the band gap of polymer **16a** in methanesulfonic acid was estimated at 2.68 eV. An optical saturation or near saturation occurred at around 400 nm. **16a** shows a narrow absorption band centering at 400 nm, while **16b** shows a broad absorption band centering at around 350 nm with a shoulder at 400 nm. This indicates that the interfacial polycondensation reaction in ethanol gives polymer **16a** with a uniform molecular weight distribution, while the solution polymerization in DMF gives polymer **16b** with a broad molecular weight distribution.

Photoluminescence Properties. The photoluminescence spectra of the oligomers and the polymers in the diluted solution of methanesulfonic acid are shown in Figures 7 and 8. All the oligomers and the polymers have similar emission bands with the maxima at 490−505 nm. These results indicate that there is little effect of the chain length on the solution luminescence of the protonated oligomers and the polymers. Large excitation and emission energy differences were observed for the oligomers and polymers in solution. From the dimer to the polymer, the Stokes shifts between the excitation and emission decreased from 122 to 95 nm (Table 2).

Viscosity and Molecular Weight of the Polymers. The viscosities of the poly(bibenzimidazole) (**16a**−**d**) were determined in methanesulfonic acid at 30.00 °C (Figure 9, Table 3). (The plots of **16b**−**d** are similar to the plot of **16a** shown in Figure 9.) The inherent viscosity η_{inh} is 0.705 and 0.553 dL/g at a concentration of 0.400 g/dL for

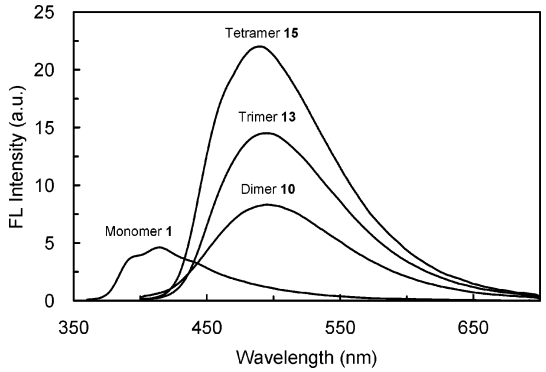

FIGURE 7. Photoluminescence spectra of the oligomers in methanesulfonic acid based on the same molar concentration (5.7×10^{-8} mol/L). (The excitation wavelength was 340 nm for the monomer, 373 nm for the dimer, 382 nm for the trimer, and 389 nm for the tetramer.)

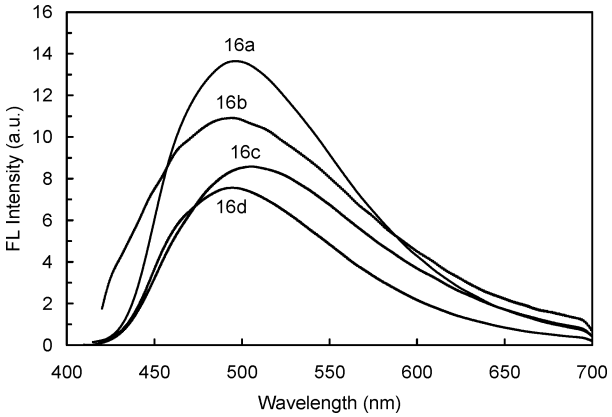

FIGURE 8. Photoluminescence spectra of the polymers **16a**−**d** in methanesulfonic acid. (The excitation wavelength was 400 nm for polymers **16a,b**, 388 nm for polymer **16c**, and 397 nm for polymer **16d**.)

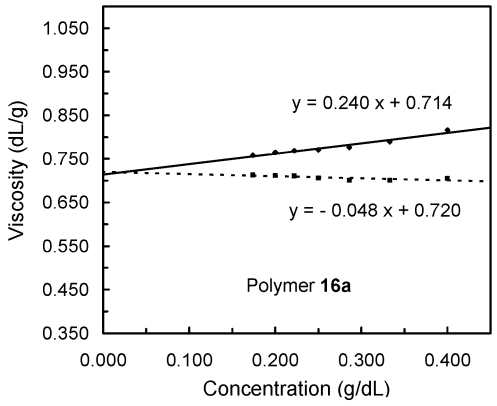

FIGURE 9. Plots of inherent viscosity η_{inh} and reduced specific viscosity η_{sp}/c vs concentration of poly(bibenzimidazole) (**16a**) at 30.00 °C in methanesulfonic acid. Solid line: $\eta_{red} = \eta_{sp}/c$. Dotted line: $\eta_{inh} = (\ln\eta_r)/c$.

16a and **16b**, respectively. The intrinsic viscosity [η] of **16a** is 0.720 dL/g, and [η] of **16b** is 0.521 dL/g obtained by extrapolating to zero concentration.[36] The number average molecular weight (M_n) of **16a** can be roughly estimated to be around 19 000, and the M_n of **16b** is around 15 000 based on the molecular weight-inherent viscosity relationship established for poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole].[10] The inherent viscosity η_{inh} is 0.425 and 0.287 dL/g at a concentration of 0.400 g/dL for **16c** and **16d**, respectively. The intrinsic viscosity [η] of **16c** is 0.387 dL/g, and [η] of **16d** is 0.344 dL/g obtained by extrapolating to zero concentration. The number average molecular weight (M_n) of **16c** can be roughly estimated to be around 9600, and the M_n of **16d** is around 6400.

TABLE 3. Viscosities of the Polymers 16a−d in Methanesulfonic Acid

entry	η_{inh} (dL/g) at 0.400 g/dL	[η] (dL/g)	M_n
polymer **16a**	0.705	0.720	19000
polymer **16b**	0.553	0.521	15000
polymer **16c**	0.425	0.387	9600
polymer **16d**	0.287	0.344	6400

TABLE 4. Thermostability of the Oligomers and Polymers

entry	onset of decomposition temp (T_d, °C)	residue at 800 °C (%)
dimer **10**	516	17.44
trimer **13**	561	52.78
tetramer **15**	572	59.30
polymer **16a**	656	47.39
polymer **16b**	646	50.80
polymer **16c**	639	54.90
polymer **16d**	662	68.98

Infrared Analysis of the Polymers. The infrared spectra of a variety of polybenzimidazoles have been discussed previously.[25,37,38] The characteristic infrared peaks of the benzimidazoles were observed in this oligomers and polymer series. In the spectral region between 3500 and 2500 cm^{-1}, a very broad peak was observed. A relatively sharp peak at 3403 cm^{-1} was attributed to the stretching absorption of isolated, non-hydrogen-bonded N−H groups. The very broad, asymmetric absorption, approximately centered at 3145 cm^{-1}, was assigned to hydrogen-bonded N−H groups. The low intensity peak at 3053 cm^{-1} was attributed to the stretching modes of the aromatic C−H groups.

The region at 1660−1480 cm^{-1} is very characteristic of benzimidazoles. The C═C/C═N stretching vibrations (1622 cm^{-1}) were observed in this region, as well as ring modes which are characteristic of the conjugation between the benzene and the imidazole rings (1585 cm^{-1}). Strong absorptions due to in-plane ring modes are found at 1422 and 1397 cm^{-1}. An imidazole ring-breathing mode gives rise to a peak at 1280 cm^{-1}. The in-plane C−H bending bands, characteristic of substituted benzimidazoles, are found at 1230−1090 cm^{-1}. For the benzene C−H out-of-plane bending modes, typically the trisubstituted benzene ring modes can be observed in the range of 950−675 cm^{-1}, especially at 947 and 802 cm^{-1}.

(36) Huggins, M. L. *J. Am. Chem. Soc.* **1942**, *64*, 2716−2718.

(37) Chen, C. C.; Wang, L. F.; Wang, J. J.; Hsu, T. C.; Chen, C. F. *J. Mater. Sci.* **2002**, *37*, 4109−4115.

(38) Guerra, G.; Choe, S.; Williams, D. J.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1988**, *21*, 231−234.

Polymers **16c**,**d** made by the reaction of 3,3′-diaminobenzidine (**9**) and bis-trichloride **14** show the characteristic IR peaks described above. In addition, they show weak absorption at around 1670 cm^{-1}, which might be due to the formation of the amide functionality in the polymer chain or at the end groups by hydrolysis in the presence of base and ethanol.[30]

Thermostability. The oligomers and the polymers are thermally stable (Table 4). The onset decomposition temperatures (T_d) are all higher than 500 °C. With the chain length increase, the T_d increases.

Conclusions

The oligomers of bibenzimidazole (dimer, trimer, and tetramer) were first synthesized using a concise and efficient synthetic strategy. This methodology is very practical overall, requires few synthetic steps, and is suitable for the synthesis of the bibenzimidazole polymers. The X-ray structure of the dimer shows that it is coplanar and centrosymmetric. This series of oligomers provided useful information for the analysis of the polymers. The UV−vis spectra show that the chain extension results in a decrease of the HOMO−LUMO gap, and the maximum absorption saturates at around 400 nm. The optical band gap of the polymer was estimated to be 2.68 eV.

The synthesis and properties of the metal complexes of the oligomers and the polymers are under investigation.

Experimental Section

2-Trichloromethylbenzimidazole (4). This is a known compound,[30] but NMR data was not reported. To a cooled suspension of the *o*-phenylenediamine (**3**) (5.41 g, 0.05 mol) and glacial acetic acid (100 mL), methyl 2,2,2-trichloroacetimidate (**2**) (8.82 g, 6.19 mL, 0.05 mol) was added slowly. When the resultant exothermic reaction subsided, the reaction mixture was kept at the room temperature for 10 h. The precipitated white powdered 2-trichloromethylbenzimidazole (**4**) was collected by filtration, washed with a small amount of water, and vacuum-dried at 50 °C for 15 h. Yield: 85%. ^{1}H NMR (500 MHz, CF_3COOD): 7.94 (dd, J = 6.6, 3.3 Hz, 2H), 7.85 (dd, J = 6.6, 3.3 Hz, 2H). ^{13}C NMR (125 MHz, CF_3COOD): δ = 149.6, 132.4, 131.8, 116.7, 83.6. ESI-MS (*m*/*z*): 234 $[M - H]^+$. IR (KBr pellet, cm^{-1}): 3500−2500 broad (3061, 2983, 2908, 2829, 2724, 2658, 2603, 2478), 1620, 1590, 1448, 1428, 1309, 1278, 1228, 1043, 892, 816, 741, 683, 501.

Bis(2,2′-bibenzimidazole)·1.5H$_2$O (10). In a suspension of 3,3′-diaminobenzidine (**9**) (1.24 g, 5.8 mmol), 2-trichloromethylbenzimidazole (**4**) (3.00 g, 12.7 mmol), and absolute ethanol (50 mL), triethylamine (5.86 g, 58 mmol) was added dropwise. The suspension was stirred at room temperature for 12 h and then refluxed under nitrogen for 36 h. The precipitated bis(2,2′-bibenzimidazole) ([bis($BiBzImH_2$)]) was collected by filtration and washed with hot glacial acetic acid. Then it was stirred in diluted ammonium hydroxide solution to neutralize the acid residue. The final product was a yellow powder. Yield: 70%. (DMF can also be the solvent to replace ethanol. If DMF is used as the solvent, then 10 equiv of absolute ethanol is needed to facilitate the reaction. The reaction in DMF was stirred at room temperature under nitrogen for 5−10 h and then heated at 75−80 °C for 24 h. The produced dimer is soluble in DMF and can be precipitated by adding water dropwise to the DMF solution. The final product was collected by filtration.) ^{1}H NMR (500 MHz, CF_3COOD): δ = 8.43 (s, 2H), 8.29 (d, J = 8.8 Hz, 2H), 8.26 (d, J = 8.8 Hz, 2H), 8.12 (dd, J = 6.6, 3.3 Hz, 4H), 7.94 (dd, J = 6.6, 3.3 Hz, 4H). ^{13}C NMR (125 MHz, CF_3COOD): δ = 144.0, 135.3, 134.8, 134.3, 134.1, 133.7, 132.5, 132.3, 118.2, 117.0, 116.1. ^{13}C NMR (125 MHz, D_2SO_4) (for comparison with the spectra of trimer, tetramer, and polymers): δ = 143.1, 133.0, 132.6, 132.5, 132.3, 132.2, 130.5, 117.5, 116.4, 116.3, 115.3, 115.2. ESI-MS (*m*/*z*): 467.2 $[M + H]^+$. IR (KBr pellet, cm^{-1}): 3500−2500 broad (3350, 3203, 3052), 1650, 1619, 1586, 1560, 1520, 1447, 1315, 1276, 809, 740. Anal. Calcd for $C_{28}H_{18}N_8 \cdot 1.5H_2O$: C, 68.14; H, 4.29; N, 22.71. Found: C, 67.60; H, 3.79; N, 22.27.

[(4-(2-(1*H*-Benzo[*d*]imidazol-2-yl)-1*H*-benzo[*d*]imidazol-5-yl)benzene-1,2-di amine)] (Compound 11). 3,3′-Diaminobenzidine (**9**) (4.00 g, 19 mmol) was dissolved in 200 mL of DMF. 2-Trichloromethylbenzimidazole (**4**) (2.00 g, 8.6 mmol) was dissolved in 45 mL of DMF and added dropwise to the above solution, followed by addition of absolute ethanol (2.5 mL). Triethylamine (6 mL) was added dropwise to the above solution. The solution was stirred at room temperature for 5 h and heated at 75−80 °C under nitrogen for 7−10 h. The reaction mixture was cooled and filtered to remove the small amount of dark brown impurity. To the filtrate, 150 mL of water was added to precipitate the solid, which was bis(2,2′-bibenzimidazole) ([bis($BiBzImH_2$)]) (**10**) (0.40 g, 0.857 mmol, yield 20%). Then to the filtrate of the above solution after **10** was removed by filtration, around 600 mL of water was added to precipitate compound **11** (1.86 g, 5.46 mmol, yield 63%). In total, 7.17 mmol of 2-trichloromethylbenzimidazole (**4**) was consumed to form compounds **10** and **11**. The overall yield is 83% based on the consumed 2-trichloromethylbenzimidazole. Product **11** can be further purified as follows: dissolve 100 mg of crude sample in 15 mL of DMF, then add 30 mL of water dropwise to precipitate the desired product. The collected solid was washed with 300 mL of water (3×) to remove DMF and dried in a vacuum oven for 20 h at 60 °C. The final product **11** was a yellow powder. ^{1}H NMR (500 MHz, CF_3COOD): δ = 8.33 (s, 1H), 8.26 (d, J = 1.65 Hz, 1H), 8.24 (d, J = 8.8 Hz, 1H), 8.12 (dd, J = 8.8, 1.7 Hz, 1H), 8.09 (dd, J = 6.6, 3.3 Hz, 2H), 8.09 (d, J = 8.3 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.92 (dd, J = 6.6, 3.3 Hz, 2H). ^{13}C NMR (125 MHz, CF_3COOD): δ = 145.6, 142.0, 135.6, 134.9, 134.6, 134.0, 133.7, 132.9, 132.5, 131.4, 129.6, 127.9, 126.8, 126.0, 118.3, 117.0, 115.7. ESI-MS (*m*/*z*): 341 $[M + H]^+$. IR (KBr pellet, cm^{-1}): 3500−2500 broad (3345, 3177, 3058, 2970), 1621, 1587, 1524, 1424,1399, 1337, 1274, 805, 766, 748, 738. Anal. Calcd for $C_{20}H_{16}N_6 \cdot H_2O$: C, 67.02; H, 5.06; N, 23.45. Found: C, 67.65; H, 4.75; N, 23.89.

Byproduct (12). The following is the procedure for the formation of compound **12** as a byproduct. 3,3′-Diaminobenzidine (**9**) (4.00 g, 19 mmol) was dissolved in 150 mL of DMF. 2-Trichloromethylbenzimidazole (**4**) (1.76 g, 7.50 mmol) was dissolved in 20 mL of DMF and added dropwise to the above solution, followed by the addition of absolute ethanol (3 mL, around 6.8 equiv). Triethylamine (7 mL, around 6.7 equiv) was added dropwise to the above solution. The solution was stirred at room temperature for 6 h and heated at 130 °C under nitrogen for 44 h. The reaction mixture was cooled and filtered to remove the small amount of dark brown impurity. To the filtrate, 200 mL of water was added to precipitate the solid, which was bis(2,2′-bibenzimidazole) (**10**) (0.300 g, 0.643 mmol). Then, to the filtrate of the above solution after **10** was removed by filtration, around 200 mL of water was added dropwise to precipitate compound **12** (1.17 g, 3.34 mmol). Then, to the filtrate of the above solution after **12** was removed by filtration, around 200 mL of water was added dropwise to precipitate compound **11** (1.85 g, 5.43 mmol). In total, 6.73 mmol of 2-trichloromethylbenzimidazole (**4**) was consumed to form compounds **10** and **11**. The overall yield is 89% based on the consumed 2-trichloromethylbenzimidazole (**4**). Product **12** can be further purified by dissolving 100 mg of the crude sample in 15 mL of DMF. Then 20 mL of water is added dropwise to precipitate the desired product. The product was washed with 300 mL of water (3×) to remove DMF and dried in a vacuum oven at 70 °C for 20 h. The final product **12** was a beige-colored

powder. ^{1}H NMR (500 MHz, CF_3COOD): δ = 9.25 (s, 1H), 8.35 (s, 1H), 8.25 (d, J = 8.6 Hz, 1H), 8.24 (s, 1H), 8.20 (d, J = 8.6 Hz, 1H), 8.11 (dd, J = 6.1, 3.1 Hz, 2H), 8.10 (d, J not determined due to the overlap, 2H), 7.93 (dd, J = 6.1, 3.1 Hz, 2H). ^{13}C NMR (125 MHz, CF_3COOD): δ = 144.7, 142.0, 141.4, 141.3, 135.0, 134.7, 134.0, 133.9, 133.7, 132.7, 132.5, 132.4, 132.3, 132.2, 130.1, 117.3, 117.0, 115.8. ESI-MS (m/z): 351 $[M + H]^+$. IR (KBr pellet, cm^{-1}): 3500−2500 broad (3048, 2968, 2887, 2794), 1398, 1377, 1344, 1282, 948, 812, 738. Anal. Calcd for $C_{21}H_{14}N_6$: C, 71.99; H, 4.03; N, 23.99. Found: C, 71.38; H, 4.08; N, 23.60.

Tris(2,2′-bibenzimidazole) (13). Compound **11** (0.20 g, 0.588 mmol) was suspended in 20 mL of absolute ethanol and stirred at room temperature for 1 h. Methyl 2,2,2-tricholoacetimidate (**2**) (0.060 g, 0.294 mmol, 0.04 mL) was added by syringe dropwise. The above suspension was stirred at room temperature for 23 h and filtered to collect the solid. The crude product was purified by heating in 50 mL of ethylene glycol at 145 °C for 24 h to remove the soluble impurities. After the suspension was cooled to room temperature, the brownish yellow trimer was collected by filtration, washed with water, and dried under vacuum at 60 °C for 40 h. Yield: 72%. ^{1}H NMR (500 MHz, CF_3COOD): δ = 8.43 (s, 4H), 8.29 (dd, J = 8.8 Hz, 3.3 Hz, 4H), 8.26 (dd, J = 8.8 Hz, 3.3 Hz, 4H), 8.11 (dd, J = 6.6, 3.3 Hz, 4H), 7.93 (dd, J = 6.6, 3.3 Hz, 4H). ^{13}C NMR (125 MHz, D_2SO_4; **13** dissolves well in D_2SO_4 but does not dissolve well in CF_3COOD, so the ^{13}C NMR spectrum was taken in D_2SO_4): δ = 143.2, 143.0, 133.1, 133.0, 132.5, 132.4, 132.3, 132.2, 131.8, 130.6, 117.4, 116.3, 115.3. ESI-MS (m/z): 699 $[M + H]^+$ (CF_3COOH as solvent for ESI). IR (KBr pellet, cm^{-1}): 3500−2500 broad (3402, 3057, 2965, 2858, 2774), 1622, 1585, 1422, 1396, 1372, 1335, 1280, 947, 810, 783, 745. Anal. Calcd for $C_{42}H_{26}N_{12}\cdot 2H_2O$: C, 68.65; H, 4.12; N, 22.88. Found: C, 68.85; H, 3.88; N, 21.91.

Bis(2-trichloromethylbenzimidazole) (14). To a solution of the 3,3′-diaminobenzidine (**9**) (2.14 g, 0.01 mol) and glacial acetic acid (50 mL), methyl 2,2,2-trichloroacetimidate (**2**) (4.41 g, 3.10 mL, 0.025 mol) was added dropwise. The reaction mixture was kept at room temperature for around 15 h. The precipitated pale yellow product bis(trichloride) **14** was collected by filtration and washed with a small amount of water. Yield: 85%. ^{1}H NMR (500 MHz, DMSO-d_6): 7.93 (s, 2H), 7.78 (d, J = 8.7 Hz, 2H), 7.71 (d, J = 8.7 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 151.2, 138.8, 137.8, 136.9, 123.7, 116.9, 114.2, 88.7. ^{13}C NMR (125 MHz, CF_3COOD): δ = 150.8, 143.5, 133.3, 132.5, 131.6, 117.8, 116.1, 83.5. ESI-MS (m/z): 431 $[M - Cl + H]^+$. IR (KBr pellet, cm^{-1}): 3500−2500 broad (3427, 3075, 2916, 2823), 1626, 1584, 1419, 1293, 1206, 1028, 876, 815, 776, 679, 514. Anal. Calcd for $C_{16}H_8Cl_6N_4$: C, 40.98; H, 1.72; N, 11.95. Found: C, 40.62; H, 1.62; N, 11.82.

Tetra(2,2′-bibenzimidazole)·2.5H$_2$O (15). To a suspension of compound **11** (0.700 g, 2.05 mmol) in 40 mL of DMF, bis(trichloride) **14** (0.385 g, 0.82 mmol) and absolute ethanol (0.50 mL) were added, followed by the dropwise addition of triethylamine (0.83 g, 8.20 mmol, 1.15 mL). The suspension was stirred at room temperature for 10 h and then heated at 75 °C under nitrogen for 34 h. The precipitated yellow tetra-(2,2′-bibenzimidazole) ([tetra($BiBzImH_2$)]) (**15**) was collected by filtration and washed with water. Then it was heated in 90 mL of ethylene glycol or DMF at around 130 °C for 24 h to remove the soluble impurities. After the suspension was cooled to room temperature, the product was collected by filtration and washed with 300 mL of water (3×). The final product was a brownish yellow powder after vacuum-drying at 70 °C for 40 h. Yield: 60%. The NMR solvent was a combination of CF_3COOD/D_2O, since [tetra($BiBzImH_2$)] does not dissolve well in CF_3COOD. ^{1}H NMR (500 MHz, CF_3COOD/D_2O): δ = 8.47 (s, 2H), 8.45 (s, 2H), 8.44 (s, 2H), 8.25 (multiplet, 12H), 8.11 (dd, J = 6.6, 3.3 Hz, 4H), 7.91 (dd, J = 6.6, 3.3 Hz, 4H). ^{13}C NMR (125 MHz, CF_3COOD/D_2O) (some peaks are overlapped and show multiplets, and some peaks are overlapped with CF_3COOD between δ 120−113 ppm): δ = 143.6, 135.2, 135.0, 134.9, 134.4, 134.3, 133.9, 133.7, 132.1, 131.8, 116.8. ^{13}C NMR (125 MHz, D_2SO_4; the tetramer dissolves well in D_2SO_4 but does not dissolve well in CF_3COOD, so the ^{13}C NMR spectrum was taken in D_2SO_4 for comparison): δ = 143.3, 143.2, 133.2, 133.1, 132.7, 132.6, 132.5, 132.4, 132.0, 130.6, 117.6, 116.5, 116.4, 115.5, 115.3. ESI-MS (m/z): 931 $[M + H]^+$ (CF_3COOH as solvent for ESI). IR (KBr pellet, cm^{-1}): 3500−2500 broad (3411, 3058, 2970, 2863, 2779), 1622, 1585, 1422, 1396, 1372, 1335, 1280, 947, 814, 783, 749. Anal. Calcd for $C_{56}H_{34}N_{16}\cdot 2.5H_2O$: C, 68.91; H, 4.03; N, 22.96. Found: C, 69.09; H, 3.69; N, 22.81.

Poly(2,2′-bibenzimidazole) (16a). 3,3′-Diaminobenzidine (**9**) was purified following the known procedures by making the tetrahydrochloride salt of it and regenerating it into the pure 3,3′-diaminobenzidine using 5% NaOH solution.[24] The slightly pink 3,3′-diaminobenzidine (**9**) (500 mg, 2.33 mmol) was suspended in 50 mL of absolute ethanol, and the solution was degassed under nitrogen for 10 min. Methyl 2,2,2-trichloroacetimidate (**2**) (411 mg, 0.288 mL, 2.33 mmol) was added dropwise. The reaction suspension was stirred at room temperature for 26 h and then refluxed for 82 h. After the suspension was cooled to room temperature, the precipitated orange brown polymer was collected by filtration. Then it was stirred in 300 mL of deionized water (3×) for around 15 h each time to remove solvent ethanol. The final orange brown polymer was collected by filtration and dried under vacuum oven at 70 °C for 80 h. Yield: 70%. It is partially soluble in concentrated sulfuric acid, methanesulfonic acid, and HCOOH and not soluble in CF_3COOH, DMAC, DMF, DMSO, and NMP. The NMR spectra were taken in D_2SO_4, due to the low solubility in CF_3COOD. ^{1}H NMR (500 MHz, D_2SO_4): δ = 8.48 (s), 7.92 (s, br), 7.85−7.70 (multiplet), 7.58 (weak multiplet). ^{13}C NMR (125 MHz, D_2SO_4, signals were relatively weak compared to those of the ^{13}C NMR of polymer **16d**, due to the lower solubility of **16a**): δ = 143.3 (br), 133.1, 132.5 (br), 131.8, 131.4, 131.0, 117.5 (br), 115.3 (br). FTIR (KBr pellet, cm^{-1}): 3500−2500 (broad), 1624, 1585, 1420, 1394, 1275, 947, 804. Anal. Calcd for $(C_{14}H_8N_4\cdot H_2O)_n$: C, 67.19; H, 4.03; N, 22.39. Found: C, 66.53; H, 3.73; N, 21.95.

Poly(2,2′-bibenzimidazole) (16b). The slightly pink, purified 3,3′-diaminobenzidine (**9**) (700 mg, 3.27 mmol) was dissolved in 50 mL of DMF, and the solution was degassed under nitrogen for 15 min. Methyl 2,2,2-trichloroacetimidate (**2**) (576 mg, 0.404 mL, 3.27 mmol) was added dropwise, followed by the addition of absolute ethanol (1.9 mL, 33 mmol). The deep orange brown reaction solution was stirred at room temperature for 54 h and then heated at 60−70 °C for 40 h. After the mixture was cooled to room temperature, the precipitated orange brown polymer was collected by filtration. Then it was stirred in 300 mL of deionized water (3×) for around 1 day each time to remove solvent DMF. The final orange brown polymer was collected by filtration and dried under vacuum at 70 °C for 80 h. Yield: 60%. It is partially soluble in concentrated sulfuric acid, methanesulfonic acid, and HCOOH and not soluble in CF_3COOH, DMAC, DMF, DMSO, and NMP. The NMR spectra were taken in D_2SO_4, due to the low solubility in CF_3COOD. ^{1}H NMR (500 MHz, D_2SO_4): δ = 8.46 (s), 7.92−7.57 (multiplet, br).^{13}C NMR (125 MHz, D_2SO_4): not obtained due to the low solubility. FTIR (KBr pellet, cm^{-1}): 3500−2500 (broad), 1624, 1585, 1420, 1394, 1275, 947, 804. Anal. Calcd for $(C_{14}H_8N_4\cdot 1.5H_2O)_n$: C, 64.86; H, 4.28; N, 21.61. Found: C, 64.48; H, 3.60; N, 21.11.

Poly(2,2′-bibenzimidazole) (16c). The slightly pink, purified 3,3′-diaminobenzidine (**9**) (365.5 mg, 1.706 mmol) was dissolved in 50 mL of DMF, and the solution was degassed under nitrogen for 15 min, followed by the addition of absolute ethanol (2 mL, 34 mmol). Bis(trichloride) (**14**) (800.0 mg, 1.706 mmol) was added in one portion. Then triethylamine (4.75 mL, 34 mmol) was added dropwise to the above solution over 10 min. (After around 4 equiv of triethylamine was added, the reaction mixture became gel-like and difficult to stir, with the formation of precipitate.) The color of the mixture was brown-

ish orange. The reaction mixture was stirred at room temperature for 8 h, then heated at 70−75 °C. The precipitate was almost completely dissolved after 8 h at 75 °C. The mixture was kept at 70−75 °C for a total of 72 h and then cooled. The orange polymer was precipitated out from the reaction mixture by the addition of deionized water and collected by filtration. Then it was stirred in 300 mL of deionized water (3×) for around 1 day each time to remove DMF. The final orange powdered polymer was collected by filtration and dried under vacuum at 70 °C for 80 h. Yield: 83%. It is soluble in concentrated sulfuric acid, methanesulfonic acid, HCOOH, CF_3COOH, DMAC, DMF, DMSO, and NMP. ^{1}H NMR (500 MHz, D_2SO_4): δ = 8.49 (s), 7.93−7.50 (multiplet, br).^{13}C NMR (125 MHz, D_2SO_4): δ = 143.2, 140.2 (br, weak), 133.1, 132.6 (br), 132.4, 131.9, 131.4, 127.8, 117.6, 116.6, 115.3. FTIR (KBr pellet, cm^{-1}): 3500−2500 broad (3060), 1624, 1585, 1420, 1379, 1334, 1283, 946, 803. Anal. Calcd for $(C_{14}H_8N_4{\cdot}H_2O)_n$: C, 67.19; H, 4.03; N, 22.39. Found: C, 67.13; H, 3.62; N, 21.61.

Poly(2,2′-bibenzimidazole) (16d). The slightly pink, purified 3,3′-diaminobenzidine (**9**) (365.5 mg, 1.706 mmol) was dissolved in 50 mL of DMF, and the solution was degassed under nitrogen for 15 min, followed by the addition of absolute ethanol (2 mL, 34 mmol). Bis(trichloride) (**14**) (800.0 mg, 1.706 mmol) was added in one portion. Then triethylamine (4.75 mL, 34 mmol) was added dropwise to the above solution over 10 min. (After around 4 equiv of triethylamine was added, the reaction mixture became gel-like and difficult to stir, with the formation of precipitate. The color of the mixture was brownish orange.) The reaction mixture was stirred at room temperature for 7 h and then heat at 75−80 °C; the precipitate was almost completely dissolved after 8 h at 78 °C. The reaction was maintained at 75−80 °C for 20 h, then heated at 120−130 °C. After around 20 h, a gray yellow precipitate formed. The mixture was heated at 120−130 °C for an additional 20 h, then heated at 145−150 °C for 46 h. After the mixture was cooled to room temperature, the precipitated greenish yellow polymer was obtained by filtration. Then it was stirred in 300 mL of deionized water (3×) for around 1 day each time to remove DMF. The final yellow powdered polymer was collected by filtration and dried under vacuum at 70 °C for 80 h in 65% yield. It is soluble in concentrated sulfuric acid and methanesulfonic acid; partially soluble in CF_3COOH and HCOOH; not soluble in DMAC, DMF, DMSO, and NMP. The NMR solvent was D_2SO_4, due to the low solubility in CF_3COOD. ^{1}H NMR (500 MHz, D_2SO_4): δ = 8.48 (s), 7.93 (s, br), 7.85−7.70 (multiplet), 7.58 (weak multiplet).^{13}C NMR (125 MHz, D_2SO_4): δ = 143.2 (br), 140.3 (br, weak), 133.1, 132.6 (br), 132.4, 131.9, 131.4, 131.0, 129.3, 117.6, 116.7, 115.3, 114.8. FTIR (KBr pellet, cm^{-1}): 3500−2500 broad (3060), 1624, 1585, 1420, 1379, 1334, 1283, 946, 803. Anal. Calcd for $(C_{14}H_8N_4{\cdot}H_2O)_n$: C, 67.19; H, 4.03; N, 22.39. Found: C, 67.87; H, 3.54; N, 22.70.

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Supporting Information Available: ^{1}H, COSY, and ^{13}C NMR spectra of compounds **10**, **11**, and **12**; FTIR spectra of compounds **1**, **4**, **10**−**16**; X-ray crystallography data of dimer **10**; CIF files for the X-ray analysis of dimer **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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