Synthesis and Characterization of π-Conjugated Monomers for Coordination Polymers

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Abstract:

π-Conjugated monomers of substituted 1,4-phenylenediamines and 1,3-phenylenediamines derivatives were synthesized and characterized with ^{1}H NMR, ^{13}C NMR, mass spectroscopy and elemental analysis. The corresponding coordination polymers were prepared by reactions of the monomers with transition salts in various conditions.

Keywords: π-Conjugated monomers, coordination polymers, nucleophilic aromatic substitution, ligands

Introduction:

Photoinduced charge separation and long-range electron transfer are important processes related to the development of molecular electronic and solar energy conversion devices.[1] Molecular systems incorporating multivalent metals at a fixed relative distance and orientation are particularly attractive. Electronic coupling between metal centers varies strongly with the distance between the metals. It also strongly depends on the nature of the ligand bridging the two centers. It is important to design and use bridging ligands insuring as strong a coupling as possible.

The self-assembly of suitably designed organic ligands with transition-metal ions allows the generation of a wide range of polymetallic complexes. These coordination polymers are important for a construction of a variety of well defined architechteres.[2] These organized entities may present interesting physical and chemical properties and are of much current interest within metallosupramolecular chemistry due to their potential applications in materials science and engineering. Although characterization of high molecular weight Cu (II) coordination polymers with ligands containing nitrogen and carbonyl groups has been studied,[3] the corresponding polymers of metal ions with symmetry π-Conjugated ligands has rarely been reported

We herein describe the synthesis and characterization of nitrogen containing symmetry π-Conjugated ligands of di-, tri-, and tetra-substituted 2-pyrimidyl-1, 4-phenylenediamines and 1, 3-phenylenediamines derivatives. These compounds, to our knowledge, have not been reported on a viewpoint of synthesis procedures. They were used as monomers for investigation of the corresponding coordination polymer synthesis with various transition metals.

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Experimental:

Derivatives of di-, tri-, and tetra-substituted 2-pyrimidyl-1,4-phenylenediamines and 1,3-phenylenediamines were synthesized by nucleophilic aromatic substitution reactions of 2-chloropyrimidine at 180 °C. The products were characterized using ^{1}H NMR, ^{13}C NMR, mass spectroscopy and elemental analysis. The coordination polymers were prepared by slowly heating the mixture of monomer and transition metal salts to 100 °C and then slowly cooled to room temperature.

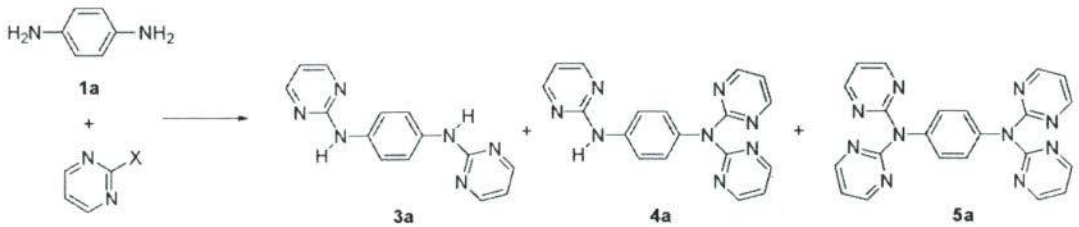
Results and Discussion:

1. Reactions of 1,4-phenylenediamine (1a) with 2-chloropyrimidine (2a)

Reactions of 1,4-phenylenediamine (**1a**) with 2-chloropyrimidine (**2a**) were carried out using various kinds of solvent and bases (Table 1). Addition of base did not promote the reactions to produce the desired tetra-substituted product; *N,N,N',N'*-Tetra(2-pyrimidyl)-1,4-phenylenediamine **5a**, whereas the reaction without base and without solvent gave higher yields of tetra-substituted product **4a** and **5a**. The reactions are more convenience for working up procedure when non-polar solvent such as *p*-Xylene or toluene was used. Consequently, the second step reaction of **3a** with 2 equivalent of 2-chloropyrimidine **2a** at 180 °C for 3 h produced higher yield of **5a** (Scheme 2). Aprotic solvents such as DMF, DMSO gave mainly di-substituted product **3a** with small amount of **4a**. Loupy and co-workers reported easy and efficient S_NAr reactions on halopyridines in solvent free conditions.[4] Thus, the reaction using KO^{t}Bu as base and tetraalkylammonium salt (Aliquat 336) as solid-liquid phase transfer catalyst (PTC) in solvent free condition at 120 °C for 6 h was examined. But only 30% of **3a** was produced. The attempted synthesis of **5a** and the meta-derivatives **5b** using Ullmann condensation methods[5,6] where copper(I) or Copper(II) and KOH were used as catalysts in toluene was unsuccessful. Only di-, and tri-substituted products were obtained without the desired tetra-substituted products from TLC measurement.

The reaction using 1,4-Diazabicyclo [2.2.2] octane as base in DMF and NaI has been carried out to examine the effective of the base. Unfortunately, none of substituted-(2-pyrimidyl)-1,4- phenylenediamine or the corresponding substituted-1,3- phenylenediamine was produced from TLC and NMR examination. Repeated purification with column chromatography did not give clean products of clearer NMR measurement.

It was found the reaction of **1a** with **2a** carried out in and ampoule and closed in an autoclave at 180 °C for 3 h produced considerably higher yields



Scheme 1 Reactions of 1,4-Phenylenediamines (1a) with 2-Chloropyrimidine (2a)

of **3a**, **4a** and **5a** (Entry 12). The reaction of **1a** with 2-Bromopyridine **2b** also gave high yields of desired products, but the reaction was not so interesting compare with using **1a** due to the drawback of expensive of **2b**. 2-Bromopyridine **2b** can be synthesized from reaction of 2-Chloropyridine **2a** with PBr_3.

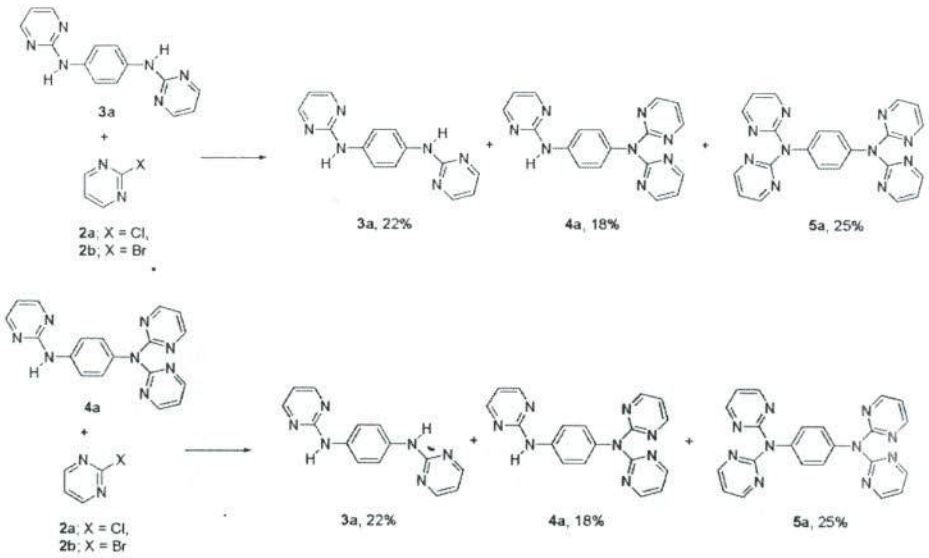
The second step reactions of **3a** or **4a** with 2 equivalent of 2-chloropyrimidine **2a** at 180 °C for 3 h gave clean reaction mixture and more convenience of work up procedure than the first step (reaction of **1a** with **2a**) and produced satisfactory yield of **5a** (Scheme 2).

Reactions of 1,4-phenylenediamine (**1a**) with 2-Bromothiazole **6** gave only *N*,*N*'-Bis(2-thiazoyl)-1,4-phenylenediamine (7) with 6% yield, whereas the reaction of **1a** with 2-Chlorobenzothiszole (**8**) gave 59% of *N*-(2-Benzothiazoyl)-1,4-phenylenediamine. Attempt to synthesize tri- and tetra-substituted (2-thiazoyl)-

Table 1 Nucleophilic Aromaric Substitution of Halopyrimidine with *p*-Phenylenediamine[a]

Entry	Solvent	Base	time	Yield (%)[b]	Product distribution[b]		
					3	**4**	**5**
1	-	K_2CO_3	3	26	16	9	1
2	-	Cs_2CO_3	3	23	20	3	-
3	-	-	3	47	30	10	7
4	*Toluene*	-	12	31	20	10	1
5	*p*-Xylene	K_2CO_3	3	30	17	13	-
6	*p*-Xylene	K_2CO_3	12	34	22	10	2
7	*p*-Xylene	K_2CO_3	24	35	13	20	2
8	Mesitylene	K_2CO_3	3	-	-	-	-
9	DMSO	K_2CO_3	3	-	-	-	-
10	DMSO	NaI/Et3N	3	-	-	-	-
11[c]	DMF	DBO/NaI	12	-	-	-	-
12[d]	-	-	3	55	14	29	12
13[e]	-	-	3	62	24	13	25

[a] Reaction conditions: [**1a**]:[**2a**]:[Base] = 1:4:4 (in mmol), solvent 2 ml, 180 °C.
[b] Isolated yields. [c] Reaction at 100 °C. DBO = 1,4-Diazabicyclo[2.2.2]octane.
[d] The reaction was carried out in an ampoule heating in an autoclave.
[e] Reaction with 2-Bromopyrimidine (**1b**).



Scheme 2 Reactions of **3a** and **4a** with 2-Chloropyrimidine **2a**

1,4-phenylenediamines, and di-, tri- and tetra-substituted (2-benzothiazoyl)-1,4-phenylenediamines was unsuccessful.

2. Reactions of 1,3-phenylenediamine (1b) with 2-chloropyrimidine (2a)

Reactions of 1,3-phenylenediamine (**1b**) with 2-chloropyrimidine (**2a**) were carried out using similar conditions as the reactions of **1a** (without solvent or base). From TLC analysis, the product selectivity was less than the reaction of **1a**, together with lower isolated product yields. Prolong reaction times gave the higher yields of all three products. Similarly to **1a**, the second step gave cleaner reaction and satisfactory product yields.

Future Outlook: The synthesized *N,N,N',N'*-Tetrakis(2-pyrimidyl)-1,4-phenylenediamine and *N,N,N',N'*-Tetrakis(2-pyrimidyl)-1,3-phenylenediamine have been subjected to the reactions with various transition metal salts to prepare the coordination polymers. The corresponding experiments are under investigation.

Conclusion:

Ligands of di-, tri-, and tetra-substituted 2-pyrimidyl-1,4-phenylenediamines and 1,3-phenylenediamines derivatives were synthesized by nucleophilic aromatic substitution reactions of 2-chloropyrimidine.

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