Research Article

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Preparation of onium salts of a reduced anthracenone crown ether macrocycle: a reactivity series involving pyridine, phosphine, thiophene, nitrile and primary amide nucleophiles

Kadarkaraisamy Mariappan, Gerald Caple, Prem N. Basa and Andrew G. Sykes*

Reaction of mineral acids with a cyclic macromolecule containing a secondary alcohol produces ammonium, phosphonium, thiophene, and amide adducts via a carbocation intermediate. X-ray crystallography confirms the structures of the products, including those when two competing nucleophiles are present. A reactivity series that mirrors the nucleophilicity index, where reactivity decreases in the order thiophene > pyridine > primary amides > alkyl nitriles >> aromatic nitriles (unreactive), results. Addition of metal ions to ammonium adducts dissolved in acetonitrile produces secondary amides via the Ritter amide synthesis. Copyright © 2012 John Wiley & Sons, Ltd.
Supporting information may be found in the online version of this paper.

Keywords: ammonium; crystallography; electrophilic addition; pyridinium; reactivity series

INTRODUCTION

We have previously reported the reaction of nitriles with compound **1** (Scheme 1, viii), which produces secondary amides in the presence of an acid catalyst.[1] The production of amides from nitriles was originally discovered by Ritter in the 1940s.[2,3] In this case however, the amide carbonyl was itself protonated and formed a stabilizing, intraannular hydrogen bond where, upon deprotonation, a large amplitude change in geometry occurred, leaving the macrocyclic pore unblocked. Unique macrocyclic end-capped oligothiophene derivatives for the colorimetric detection of Hg (II) have been reported previously using similar chemistry.[4] We have extended this chemistry to different nucleophiles, namely pyridine analogs (pyrazine, pyrimidine), phosphines, and primary amides, for the purpose of designing novel host systems for the luminescence detection of metal ions. Described within is the organic synthesis and X-ray crystallographic characterization of a series of onium and amide adducts of **1**. Of special importance are the heterocyclic adducts of **1**, which have an additional nitrogen Lewis base present that adds dimensionality to potential new hosts that could selectively bind metal ions in near proximity to the polyether ring. Whereas conversion of primary amides into secondary amides by reaction with alcohols is fairly common,[5–10] ammonium adduct formation using similar chemistry has only recently been employed in the synthesis of surfactants,[11] new ionic liquids,[12] novel heterocycles of pharmaceutical interest,[13,14] and powerful methylating agents.[15]

EXPERIMENTAL

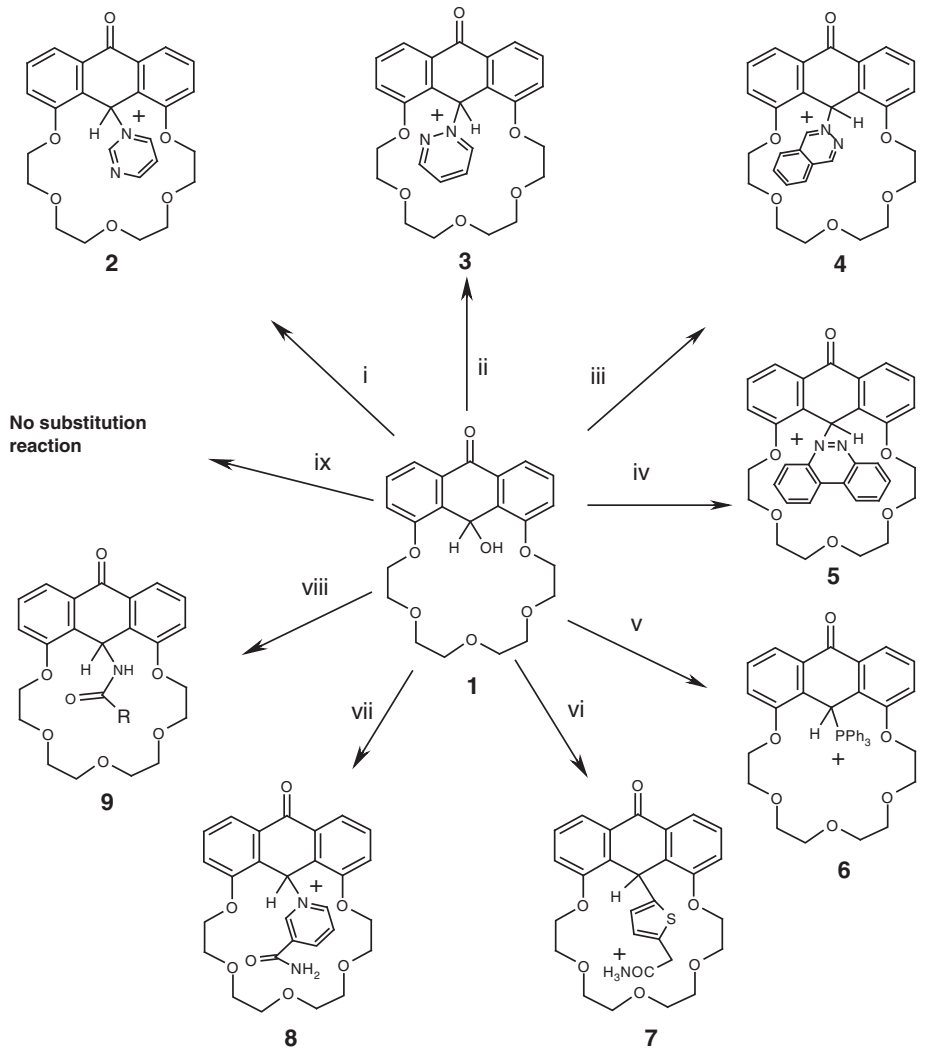
The synthesis of 1,8-oxybis(ethylenethoxyethylenethoxy)-10-hydroxy-10-hydro-9-anthracenone (**1**) has previously been reported.[1] Pyridazine, pyrimidine, phthalazine, benzo[*c*]cinnoline, triphenylphoshine, thiophene-2-acetamide, and nicotinamide were purchased from Aldrich Milwaukee, WI, USA and used without further purification. ^{1}H (200 MHz) and ^{13}C NMR (50 MHz) spectra were obtained using a Varian 200 MHz instrument Agilent Technologies, Palo Alto, CA, USA at room temperature referenced to the residual $CHCl_3$ solvent peak. Elemental analyses were conducted using an Exeter CE-440 Elemental Analyzer Chelmsford, MA, USA. Electrospray ionization mass spectrometry (ESI-MS) was conducted using a Varian 500 Mass Spectrometer. Melting points were determined in an open capillary and are uncorrected.

General synthesis – liquid precursors

1,8-Oxybis(ethylenethoxyethylenethoxy)-10-hydroxy-10-hydro-9-anthracenone (0.2 g) (**1**) was dissolved in 5 mL of pyrimidine or pyrazine and mixed with 10 drops of 70% perchloric acid. The solution turned blue/green and fades to yellow after 30 min. To this mixture was added 50 mL of diethyl ether, and a yellow-colored solid was obtained, filtered, washed with diethyl ether, and air dried.

* *Correspondence to: A. G. Sykes, Department of Chemistry, University of South Dakota, Vermillion, SD 57069, USA. E-mail: asykes@usd.edu*

K. Mariappan, G. Caple, P. N. Basa, A. G. Sykes
Department of Chemistry, University of South Dakota, Vermillion, SD, 57069, USA



Scheme 1. (i) Pyrimidine, $HClO_4$; (ii) pyridazine, $HClO_4$; (iii) phthalazine, $HClO_4/C_6H_5CN$; (iv) benzo(*c*)cinnoline, $HClO_4/C_6H_5CN$; (v) triphenylphosphine, $HClO_4/C_6H_5CN$; (vi) thiophene-2-acetamide, H_2SO_4/C_6H_5CN; (vii) nicotinamide, $HClO_4/C_6H_5CN$; (viii) alkyl nitrile, $HClO_4$; and (ix) benzonitrile, $HClO_4$. Anions have been omitted for clarity

[1-Pyrimidinium](ClO$_4$) (**2**): Yield = 20%; mp = 168–170 °C (dec.). Elemental analyses calculated for $C_{26}H_{27}N_2O_{10}Cl.CH_3CN$: C, 55.70; H, 4.96; N, 6.95%. Found: C, 55.58; H, 4.90; N, 6.82%. ESI MS calcd. for $[C_{26}H_{27}N_2O_6]^+$, M^+, 463.3. Found 462.9.

[1-Pyridazinium](ClO$_4$) (**3**): Yield = 15% mp = 185–190 °C. Elemental analyses calculated for $C_{26}H_{27}N_2O_{10}Cl$: C, 55.49; H, 4.79; N, 4.97%. Found: C, 55.24; H, 4.74; N, 5.03%. ESI MS calcd. for $[C_{26}H_{27}N_2O_6]^+$, M^+, 463.3. Found 462.6.

General synthesis – solid precursors

1 (0.5 mmol) and either phthalazine, benzo[*c*]cinnoline, or triphenylphosphine (0.55 mmol) were dissolved in 5 mL of benzonitrile and mixed with five drops of perchloric acid. The mixture was stirred for 30 min and mixed with 50 mL of diethyl ether. A tan or yellow solid was obtained, filtered, washed with diethyl ether, and air dried.

[1-Phthalazinium](ClO$_4$) (**4**): Yield = 55%; mp = >210 °C (dec.). Elemental analyses calculated for $C_{30}H_{29}O_{10}N_2Cl.0.5CH_3CN$: C, 58.67; H, 4.85; N, 5.53%. Found: C, 56.80; H, 4.68; N, 5.44%. ESI MS calcd. for $[C_{30}H_{29}O_6N_2]^+$, MH^+, 513.3. Found 514.4.

[1-Benzo[*c*]cinnolinium](ClO$_4$) (**5**): Yield = 75%; mp = 173–175 °C (dec.). Elemental analyses calculated for $C_{34}H_{31}N_2O_{10}Cl.CH_3CN$: C, 61.43; H, 4.83; N, 5.96%. Found: C, 61.11; H, 4.79; N, 5.81%. ESI MS calcd. for $[C_{34}H_{32}N_2O_6]^+$, M^+, 563.3: Found 562.8.

[1-Triphenylphosphonium](ClO$_4$) (**6**): Yield = 55%; mp = 115–118 °C. Elemental analyses calculated for $C_{40}H_{37}O_{10}ClP.2CH_3CN$: C, 63.98; H, 5.20; N, 3.39%: Found: C, 63.33; H, 5.61; N, 3.03%. ESI MS calcd. for $[C_{40}H_{37}O_6P]^+$, M^+, 644.7: Found 644.8.

Competition studies

Thiophene versus primary amide nucleophiles

1 (0.5 mmol) and thiophene-2-acetamide (0.55 mmol) were dissolved in 5 mL of benzonitrile and mixed with five drops of sulfuric acid. The mixture was stirred for 30 min and mixed with 50 mL of diethyl ether. The crude solid was dissolved in 10 mL of acetonitrile, and diethyl ether was diffused into the solution. Cream-colored crystals of (**7**), [**1**-(5-(thiophene-2-acetamide))H](HSO$_4$), were obtained in 20% yield (melting point = 220 °C (dec.)).

Pyridine versus primary amide nucleophiles

1 (0.5 mmol) and nicotinamide (0.55 mmol) were dissolved in 5 mL of benzonitrile and mixed with five drops of 70% perchloric acid. The

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mixture was stirred for 30 min and mixed with 50 mL of diethyl ether. The crude solid was dissolved in 10 mL of acetonitrile, and diethyl ether was diffused into the solution. Cream-colored crystals of [**1**-(*N*-nicotinamide)] (ClO_4) (**8**) were obtained in 30% yield (melting point = 172–175 °C).

Primary amide (benzamide) versus alkyl nitrile (acetonitrile) nucleophiles

1 (0.5 mmol) and benzamide (0.55 mmol) were dissolved in 5 mL of acetonitrile and mixed with five drops of 70% perchloric acid. The mixture was stirred for 30 min and mixed with 50 mL of diethyl ether. The crude solid was dissolved in 10 mL of acetonitrile, and diethyl ether was diffused into the solution. Cream-colored crystals (**10**) were obtained, and the unit cell is identical to the secondary amide structure we reported earlier[1] (yield: ~70%).

*Thiophene versus pyridine (benzo(c)*cinnoline) nucleophiles

1 (0.5 mmol), bithiophene (0.55 mmol), and benzo(*c*)cinnoline (0.55 mmol) were dissolved in 5 mL of benzonitrile and mixed with five drops 70% perchloric acid. The mixture was stirred for 30 min and mixed with 50 mL of diethyl ether. The crude solid was dissolved in 10 mL of acetonitrile, and diethyl ether was diffused into the solution. Both a cream-colored solid (**11**) and yellow-colored crystals (**12**) were obtained. Compound **11**, the macrocyclic end-capped bithiophene adduct (Scheme 2), has previously been reported.[4] Compound **12** is protonated benzo(*c*)cinnoline and was characterized by single-crystal X-ray analysis. Yield: ~20% of compound **11** and 30% of compound **12** (melting point: 219–222 °C).

Crystallography

X-ray quality crystals were grown from samples dissolved in acetonitrile and diffused with diethyl ether. Crystallographic data were collected at 100 K using MoKα radiation on a Bruker CCD APEXII diffractometer, Madison, WI, USA. Cell constants were determined after integration from typically more than 9000 reflections.[16] Structures were solved by direct methods using SIR97[17] and refined using SHELXL-97.[18] Data reduction and refinement were completed using the WinGX suite of crystallographic software.[19] All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters, with the exception of hydrogen-bonded protons, which were found from the difference map. Table 1 lists additional crystallographic and refinement information. Only the major occupancies of disordered structures have been diagramed in Figs. 1–3.

[1-Pyridazinium](ClO_4)·0.6H_2O (**2**): There are two pyridazinium adducts in the asymmetric unit along with one water of hydration with a 60% occupancy. One perchlorate is disordered over two separate positions in a 74:26 ratio. The major fractions of the disordered water and perchlorate participate in a hydrogen bond = 2.868(4) Å, 169(5)°.

[1-Phthalazinium](ClO_4) (**4**): One-half of the polyether chain is disordered over two positions in a 50:50 ratio.

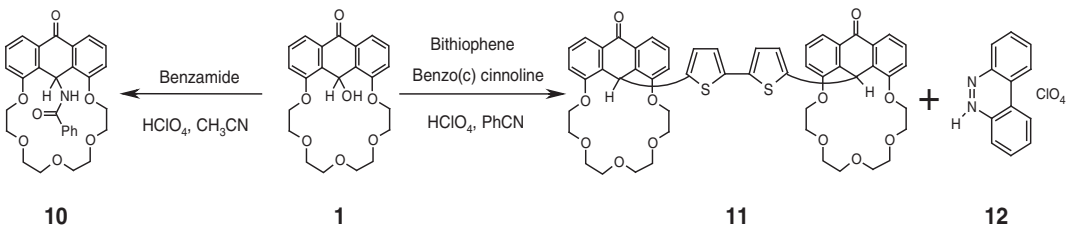
[1-Benzo[*c*]cinnolinium](ClO_4)·CH_3CN (**5**): One-half of the polyether chain is disordered in a 60:40 ratio. Refinement of the smaller occupancy was left isotropic.

[1-(5-(Thiophene-2-acetamide))H](HSO_4) (**7**): Platon Squeeze removed a disordered solvent molecule present in the structure equal to 140 $Å^3$/61 electrons.[20] This is equivalent to approximately one-half a diethyl ether molecule per asymmetric unit, which was used as the antisolvent during crystallization. The anion is also rotationally disordered over two positions in a ~60:40 ratio. The smaller occupancy was left isotropic. Because of the anion disorder, neither of the hydrogen atoms around the sulfate anion could be reliably located. SADI was used to restrain all sulfur–oxygen distances within the anions as well.

RESULTS – SYNTHESIS AND CRYSTALLOGRAPHY

Pyrimidine and pyridazine, liquids at room temperature, react in neat solution together with **1** and perchloric acid to yield the ammonium adducts **2** and **3**. Elemental analyses and mass spectrometry results are consistent with the formation of the ammonium salts. Phthalazine, benzo[*c*]cinnoline, and triphenylphosphine starting materials are solids at room temperature, so these reactants were dissolved in benzonitrile solvent (itself unreactive) before addition of **1** and $HClO_4$ to yield compounds **4–6**. Chemical structures of **2–6** were also confirmed by X-ray crystallography by recrystallization in acetonitrile diffused with diethyl ether (Figs. 1–3). All the ammonium adducts (**3**, **4**, and **5**) with two adjacent nitrogens have the uncoordinated nitrogen pointed towards the anthracenone. This eliminates steric interference that would occur between the phenyl hydrogen atom and the anthracenone if the heterocyclic ring was rotated 180° about the pyridyl C–N bond. The lower yield of products derived from neat solution is likely due to a shift in the amount of free base and acid catalyst towards the protonated salt associated with the addition of the mineral acid.

We have previously determined that thiophene groups are more susceptible to substitution at the aromatic alpha-position when in the presence of alkyl nitriles as a competing nucleophile.[4] We extend this chemistry to include competition reactions between a pyridine or thiophene group in the presence of primary amides. In either case, the primary amide is left unreacted. Reaction of thiophene-2-acetamide with **1** in the presence of sulfuric acid as catalyst produces the thiophene substituted product **7** where the anthracenone substitutes at the 2-position of the thiophene ring (crystal structure, Fig. 4). This leaves a neutral molecule; however, it appears from bond distances between heavy atoms in the crystal structure that the amide oxygen is protonated by the catalyst after the reaction is complete. The anion, hydrogen sulfate, is found rotationally disordered in a ~60:40 ratio, making it difficult to accurately locate hydrogen atoms involved in the hydrogen bonding between the anion and the amide group. However, it is apparent that a very short O. . .H–O hydrogen bond exists between the hydrogen sulfate and the amide oxygen, O7. . .O8 = 2.555(7) Å. The hydrogen bond distance for the smaller occupancy of the disordered anion is even shorter, O7. . .O8′ = 2.420 Å. A second hydrogen bond is



Scheme 2. Competition of bithiophene versus benzo(*c*)cinnoline derivative and benzamide versus acetonitrile with **1** in the presence of a strong acid

Table 1. Crystallographic and refinement data for: [**1**-pyrimidinium](ClO_4)·CH_3CN (**2**); [**1**-pyridazinium](ClO_4)·0.6H_2O (**3**); [**1**-phthalazinium](ClO_4) (**4**); [**1**-benzo(*c*)cinnolinium](ClO_4)·CH_3CN (**5**); [**1**-triphenylphosphonium](ClO_4)·2CH_3CN (**6**); [**1**-(5-thiophene-2-acetamide)H](HSO_4) (**7**); [**1**-nicotinamide](ClO_4) (**8**). [Benzo(*c*)cinnolineH](ClO_4) (**12**). **1** = 9-substituted-1, 8-oxybis(ethyleneoxyethyleneoxy)anthracence-10-one

	2	**3**	**4**	**5**	**6**	**7**	**8**	**12**
Empirical formula	$C_{28}H_{30}ClN_3O_{10}$	$C_{54}H_{55}Cl_2N_4O_{20.5}$	$C_{30}H_{29}ClN_2O_{10}$	$C_{36}H_{34}ClN_3O_{10}$	$C_{44}H_{44}ClN_2O_{10}P$	$C_{28}H_{29}NO_{11}S_2$	$C_{28}H_{29}ClN_2O_{11}$	$C_{12}H_9Cl_1N_2O_4$
Formula weight	604.00	1134.90	613.00	704.11	827.23	619.66	604.98	280.66
Temperature (K)	125(2)	125(2)	125(2)	125(2)	100(2)	100(2)	100(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P1	P1	P1	P21/n	Pc	P21/c	P21/c	P1
a (Å)	10.9002(5)	10.097(2)	10.5161(6)	13.4277(10)	12.1812(15)	11.9134(10)	9.2180(14)	7.8644(19)
b, (Å)	11.5936(5)	10.802(2)	10.9745(6)	14.6365(11)	11.2560(14)	21.6293(10)	23.226(3)	9.083(4)
c, (Å)	13.3742(6)	24.017(5)	13.9790(8)	16.7031(12)	14.9539(19)	11.4081(10)	12.3431(18)	9.094(2)
α (°)	68.857(1)	86.680(2)	106.525(1)					107.036(4)
β (°)	88.578(1)	85.093(2)	105.459(1)	100.855(1)	102.441(2)	93.346(1)	96.950(2)	107.811(3)
γ (°)	62.370(2)	81.142(2)	97.038(1)					97.209(4)
Volume ($Å^3$)	1375.7(1)	2576.0(9)	1456.0(1)	3224.0(4)	2002.2(4)	2934.6(4)	2623.2(7)	574.6(3)
Z	2	2	2	4	2	4	4	2
Density (calc.; g cm^{-3})	1.456	1.463	1.406	1.451	1.372	1.403	1.532	1.622
Absorb. coef. (mm^{-1})	0.204	0.212	0.193	0.186	0.198	0.243	0.216	0.345
F(000)	630	1186	640	1472	868	1296	1264	288
Index ranges (*hkl*)	±12 ± 13 ± 15	±12 ± 12 ± 28	±12 ± 13 ± 16	±16 ± 17 ± 20	±14 ± 13 ± 17	±14 ± 26 ± 13	±10 ± 27 ± 14	±9 ± 11 ± 11
Reflections collected	13613	25125	14821	32293	19274	29369	24947	5977
Independent reflections	4859	9070	5368	5946	7056	5404	4619	2185
Observed reflections	4178	7477	4181	4301	6415	4567	2448	1879
Max/min trans.	0.916/0.947	0.901/0.969	0.916/0.970	0.916/0.974	0.950/0.965	0.837/0.925	0.924/0.970	0.866/0.947
Param./restr.	380/0	742/1	420/0	449/0	525/2	391/12	387/0	176/0
Goodness-of-fit	1.035	1.058	1.084	1.053	1.014	1.034	1.047	1.060
Final *R* indices[$I > 2\sigma(I)$]	0.0369	0.0417	0.0465	0.0534	0.0415	0.0755	0.0585	0.0370
R indices (all data)	0.0959	0.0959	0.1229	0.1254	0.1050	0.2210	0.1100	0.0968
CCDC #	806894	806895	806897	806896	806898	806900	806899	849655

CCDC, Cambridge Crystallographic Data Centre.

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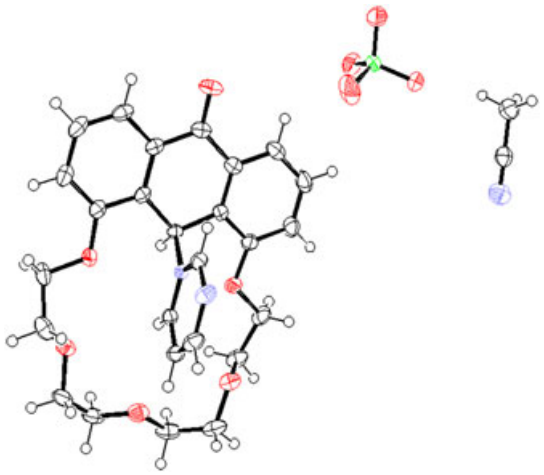


Figure 1. Thermal ellipsoid diagrams (30%) of [**1**-pyrimidinium](ClO_4)·CH_3CN (**2**)

formed between the amide hydrogen (H1B) and the anion as well, N1-H1B. . .O11 = 2.835(8) Å. A third hydrogen bond exists in the structure between the second amide hydrogen and a different neighboring anion, N1-H1A. . .O10 = 2.973(9) Å. These competing amide hydrogen bonds may produce the different occupancies of the rotationally disordered anion.

Nicotinamide contains both a heterocyclic aromatic ring and a primary amide group, and reaction with **1** yields only the ammonium ion adduct and not the amide adduct **8** (crystal structure, Fig. 5). An intramolecular hydrogen bond is formed between the amide group and one of the polyether oxygens, 2.832(5) Å, and a second intermolecular hydrogen bond forms between the second amide hydrogen and an ether oxygen of a neighboring macrocycle, 2.957(5) Å.

DISCUSSION – RELATIVE REACTIVITY

Upon addition of a strong acid with **1**, the secondary alcohol is protonated, and the loss of water produces a transient carbocation intermediate as shown in Scheme 3. Either concentrated $HClO_4$ or concentrated H_2SO_4 can generate the carbocation, but we used concentrated H_2SO_4 for the thiophene derivatives specifically because better yields are produced. In the other cases, acid choice does not make any difference. Further reaction of the short-lived carbocation with the nucleophilic pyridyl, thiophene, or phosphine lone pair produces onium and thiophene adducts as characterized previously.

We have previously demonstrated that the reaction of **1** with alkyl nitriles produces secondary amides via the Ritter amide synthesis, and that aromatic nitriles, which contain a weaker nucleophilic nitrogen, are unreactive towards **1** in the presence of a strong acid (Scheme 1, ix).[1] Earlier work also showed that activated aromatics such as pyrrole and thiophene are also more reactive than alkyl nitriles,[4] and we have now determined that pyridine analogs and thiophene are more reactive than primary

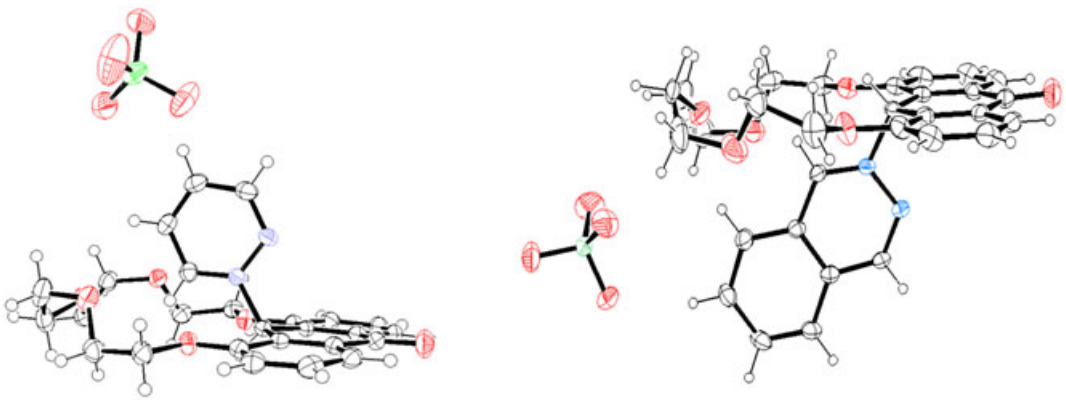


Figure 2. Thermal ellipsoid diagrams (30%) of [**1**-pyridazinium](ClO_4)·0.6H_2O (**3**) – left (the water molecule has been omitted from the diagram), and [**1**-phthalazinium](ClO_4) (**4**) – right

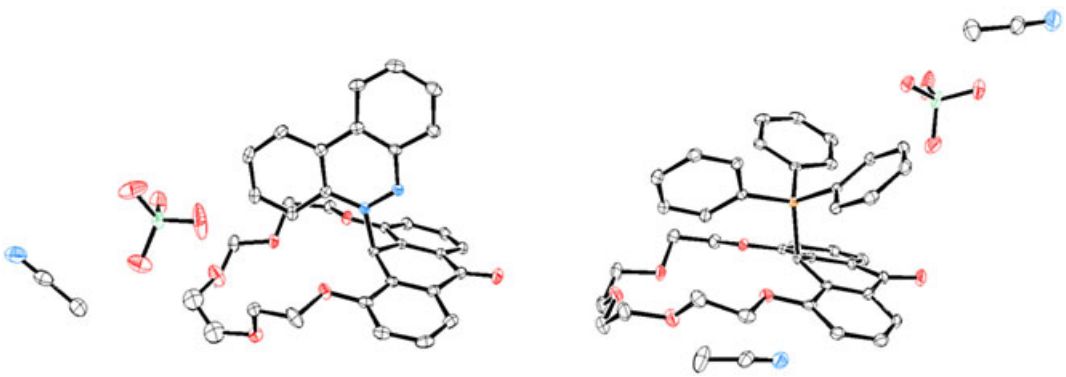


Figure 3. Thermal ellipsoid diagrams (30%) of [**1**-benzo(*c*)cinnolinium](ClO_4)·CH_3CN (**5**) – left, and [**1**-triphenylphosphonium](ClO_4)·2CH_3CN (**6**) – right. Hydrogen atoms have been removed for clarity

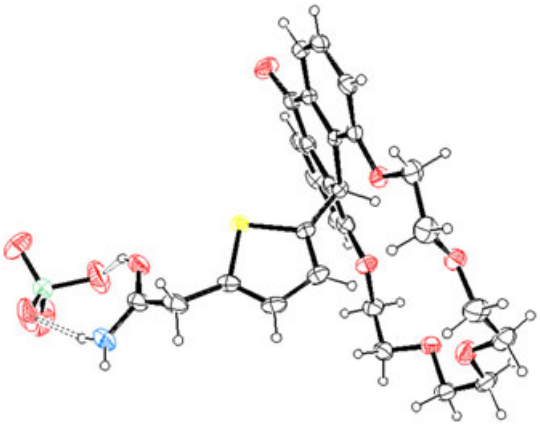


Figure 4. Thermal ellipsoid diagram (30%) of [**1**-(5-(thiophene-2-acetamide))H](HSO_4) (**7**). The thiophene group forms adduct rather than a primary amide, which is in competition as the nucleophile. In this case, the anion forms two hydrogen bonds to the amide, one via the amide oxygen, O7. . .O8 = 2.555(7) Å and a second via one of the amide hydrogen, N1-H1B. . .O11 = 2.838(8) Å. The anion is spherically disordered, but only the larger occupancy is shown

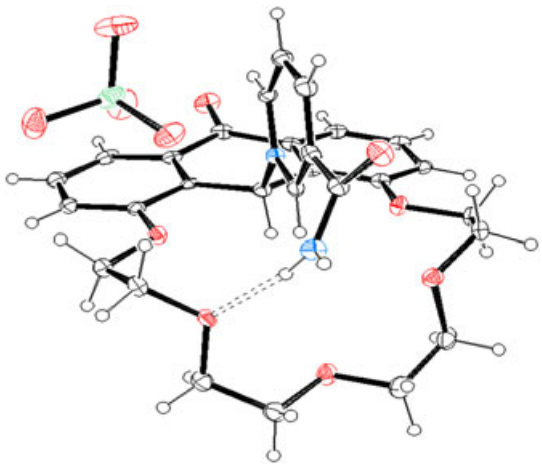


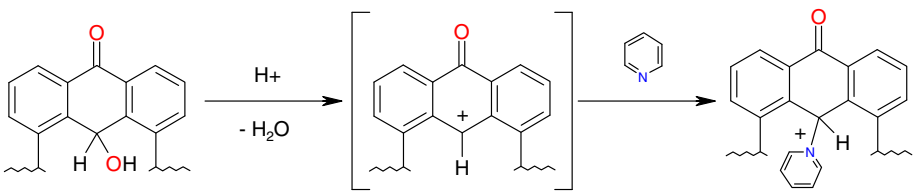
Figure 5. Thermal ellipsoid diagram (30%) of [**1**-(*N*-nicotinamide)](ClO_4) (**8**) where the ammonium adduct rather than the amide is produced. The intramolecular hydrogen bond formed has a typical N–H. . .O bond distance of 2.832(5) Å

amides because the primary amides are left unreacted in the presence of either of these other two functional groups (Scheme 1, vi and vii). In addition, we have run the competition reaction (Scheme 2) of benzamide ($C_6H_5C(O)NH_2$) with **1** in pure acetonitrile, and the only product that is formed is the secondary benzyl amide adduct, [**1**·$NHC(OH)C_6H_5$](ClO_4) (**10**). This product has been structurally characterized previously.[1] Even though the alkyl nitrile used as the solvent is by far in excess, the only product isolated is the secondary amide obtained from the primary benzamide starting material. This indicates that primary amides are more reactive than alkyl nitriles. As per Scheme 2, another competition reaction was conducted by mixing one equivalent of bithiophene with one equivalent of benzo[*c*]cinnoline with **1** in benzonitrile/70% perchloric acid. We isolated two different solids from this reaction. One is a bithiophene dimer, **1**-C_4H_2S-C_4H_2S-**1** (**11**), isolated as a powder, which was confirmed by ^1H NMR. The molecular structure of **11** has previously been reported.[4] The second yellow, crystalline product is the mono-protonated form of benzo[*c*]cinnoline which was also characterized by X-ray crystallography as [benzo(*c*)cinnolineH](ClO_4) (thermal ellipsoid diagram not shown). A 2.890(4) Å hydrogen bond exists between the protonated benzo(*c*)cinnoline nitrogen and the neighboring perchlorate anion. This experiment clearly confirms that the activated aromatics such as thiophene compete with pyridyl starting materials to form alpha-substituted thiophene products, leaving the basic pyridyl groups protonated and unreacted. The aforementioned reactions produce the following reactivity series:

thiophenes > *pyridines* > *primary amides* > *alkyl nitriles* ≫ *aromatic nitriles* (*unreactive*).

This series parallels the nucleophilic donor number for pyridine (33.1), formamide (24.0), acetonitrile (14.1), and benzonitrile (11.9), predicting that pyridine analogs are more reactive than amides, which in turn are more reactive than nitriles.[21] Although nucleophilicity is generally considered a kinetic parameter (i.e., the quality of an entering or leaving group), the substitution of thiophenes produces the most stable adducts in the end because a full covalent C–C bond is formed between the anthracenone and the heterocyclic ring. The anthracenone–ammonium C–N bond almost certainly has some coordinate-covalent character resulting in weaker bond formation. We have observed this after attempting to coordinate metal ions within macrocycles **3**, **4**, and **5**.

Our original intent was to create an internal charge transfer fluorescence sensor (Scheme 4) by coordination of metals to the second, free nitrogen atom adjacent to the polyether ring. This would tune the luminescence by altering internal charge transfer within the lumophore, depending on the identity of the metal, and would minimize vibrations that deactivate the excited state, because the pyridyl group is also coordinated to the metal. This phenomenon could be used as a novel chemodosimeter type approach for sensing metal ions. Using acetonitrile as solvent, the addition of metal ions (nonspecific) to isolated products **2–5** leads only to the production of the secondary amide adduct, (**9**), shown in Scheme 1. Through coordinate-covalent bonding, the metal likely helps dissociate the ammonium adducts into a carbocation, which is attacked by the nitrile group of the solvent, present in high concentration, followed by rearrangement via the Ritter amide synthesis to yield a secondary amide. We are currently pursuing the luminescence sensor



Scheme 3. General mechanism of carbocation generation and onium ion formation

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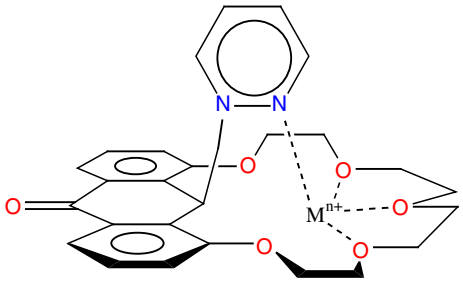

Scheme 4. Proposed metal ion coordination to an ammonium adduct of **1**

chemistry of the aforementioned ammonium adducts in different solvents that allow adequate solubility, but are not reactive, and these details will be reported elsewhere.

SUPPORTING INFORMATION

Crystallographic files in CIF format can be obtained free of charge from the Cambridge Crystallographic Data Center, www.ccdc.cam.ac.uk/conts/retrieving.html.

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