

Linear 6,6'-Biazulenyl Framework Featuring Isocyanide Termini: Synthesis, Structure, Redox Behavior, Complexation, and Self-Assembly on Au(111)

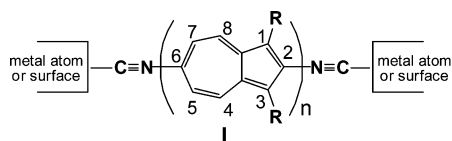
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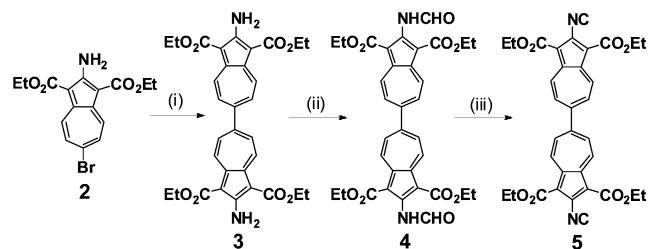
Abstract: The key step in accessing the title species (**5**), the first nonbenzenoid diisocyanobiaryl, involved an unexpected homocoupling of a 6-bromoazulene derivative. The reversible $2e^-$ reduction of **5** was addressed electrochemically and computationally. The shifts in energies of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions for a series of related 6,6'-biazulenyl derivatives correlate with the e^- -donating/-withdrawing strength of their 2,2'-substituents but follow opposite trends. Species **5** adsorbs end-on (η^1) to the Au(111) surface via one of its $-NC$ groups to form a 2-nm-thick film. In addition, bimetallic coordination of **5**'s $-NC$ termini can be readily achieved.

Azulene is an unusual aromatic hydrocarbon ($C_{10}H_8$) that comprises an edge sharing combination of five- and seven-membered sp^2 -carbon rings. The azulenic and polyazulenic motifs constitute attractive building blocks in the design of redox addressable, optoelectronic, and conductive materials.^{1–4} Unlike the frontier molecular orbitals of benzenoid aromatics, the HOMO and LUMO of azulene are not mirror related and feature mutually complementary density distributions (HOMO = Highest Occupied Molecular Orbital, LUMO = Lowest Unoccupied Molecular Orbital).³ This leads to a remarkably low $S_0 \rightarrow S_1$ excitation energy for azulene derivatives and enables topological asymmetry in the electron and hole transport regimes for azulene-based frameworks.^{1–4}



Coordination and surface chemistry of linear benzenoid diisocyanoarenes containing one or more linked aromatic rings has been the subject of growing experimental and theoretical interest,^{5,6} particularly in the context of developing advanced materials that may support charge delocalization and transport at the nanoscale.⁷ We have recently engaged in the quest for a novel class of linear diisocyanobiazulenyl scaffolds based on the nonbenzenoid 2,6-azulenic framework as represented by the homologous series **I**.^{1,8,9} For $n = 1$ ($R = -CO_2Et$) in **I**, the orientation of the azulenic dipole can be controlled through regioselective installation and coordination of the isocyanide junction groups.⁸ For $n = 2$, three different linear diisocyanobiazulenyl scaffolds can be envisioned: two symmetric featuring the 6,6' or 2,2' connectivity of the azulenic moieties and one asymmetric having the 2,6' central C–C bond. Currently, very few 2,2'-, 6,6'-, and 2,6'-biazulenyl derivatives are synthetically accessible.¹⁰ In this Communication, we introduce the chemistry of the first member of the linear diisocyanobiazulenyl family that

is formally derived by linking two 1,3-diethoxycarbonyl-2-isocyanobenzazulene (**1**)⁹ molecules. To the best of our knowledge, the title species is not only the first structurally characterized linear biazulenyl¹⁰ compound but also the sole example of a crystallographically addressed biazulenyl motif of any connectivity not embedded into a larger rigid framework.¹¹

Scheme 1^a

^a (i) B_2pin_2 (0.26 equiv), 10 mol % $Pd(dppf)Cl_2 \cdot CH_2Cl_2$, KOAc, DMSO, 100 °C, argon atm.; (ii) $HC(O)OAc$, 50 °C, (iii) $POCl_3$, Et_3N , 20 °C.

Combining the 6-bromoazulene derivative **2**⁸ with bis(pinacolato)diboron (B_2pin_2) in the presence of $Pd(dppf)Cl_2$ ($dppf$ = bis(diphenylphosphino)ferrocene) under the conditions specified in Scheme 1 afforded brick-red 2,2'-diamino-6,6'-biazulenyl **3** in a 91% yield. Surprisingly, the best yields of this unexpected, “one-pot” homocoupling of **2** were achieved by employing a substoichiometric amount (*ca.* 0.25 equiv) of B_2pin_2 . No formation of **3** was observed when the reaction was conducted in the absence of B_2pin_2 under otherwise identical conditions.¹² Interestingly, our attempts to use 0.5 equiv of B_2pin_2 (the stoichiometric quantity of B_2pin_2 typically employed in one-pot homocoupling of organohalides via sequential Miyaura borylation/Suzuki cross-coupling)¹³ invariably led to much lower yields ($\leq 37\%$) of **3**. The above quite efficient protocol for the preparation of **3** evolved from our initial efforts to improve its original synthesis by Mutaftji, Sugihara et al.^{10c} The latter involved a $Pd(dppf)Cl_2$ -catalyzed borylation of **2** with 1.1 equiv of B_2pin_2 to isolate the corresponding 6-azulenyl-boronic ester, which was then cross-coupled with **2** using a different catalyst, $Pd(PPh_3)_2Cl_2$, to give **3** in a 17% overall yield.^{10c}

Formylation of **3** with acetic-formic anhydride afforded a 79% yield of sparingly soluble chestnut-colored 2,2'-diformamido-6,6'-biazulenyl **4**, the double dehydration of which gave lavender needles of 2,2'-diisocyanobenzazulene-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulenyl **5** in a 34% isolated yield. The FTIR and ^{13}C NMR spectra of **5** exhibit signature peaks at $\nu_{C\equiv N} = 2130\text{ cm}^{-1}$ (in Nujol mull) and $\delta = 178.6\text{ ppm}$ (in $CDCl_3$), respectively, that correspond to the isocyanide termini of this air-stable compound.

It is well argued that varying the nature of the substituent in a 2-substituted azulene chiefly affects the energy of its LUMO but not HOMO.³ The λ_{max} value for the relatively weak $S_0 \rightarrow S_1$ transition

in the electronic spectra of **3**, **4**, and **5** in CH_2Cl_2 appears to increase upon proceeding from **3**¹⁴ to **4** (474 nm) to **5** (509 nm). This trend parallels the order of decreasing e^- -donating/increasing e^- -withdrawing strength of the groups at the 2,2'-positions in these 6,6'-biazulenyls: $\text{NH}_2 > -\text{NHCHO} > -\text{N}\equiv\text{C}$. At the same time, however, λ_{max} of the more intense higher energy band, which we tentatively assign as $S_0 \rightarrow S_2$, increases in reverse order **5** (390 nm) < **4** (421 nm) < **3** (459 nm). Thus, the 2,2'-substitution of the 6,6'-biazulenyl scaffold provides an opportunity to simultaneously tune the wavelengths of both $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitations in mutually opposing directions in the visible region.

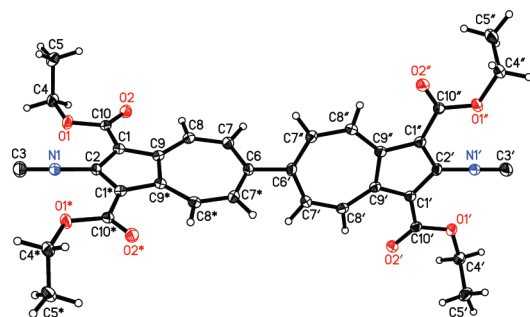


Figure 1. Molecular structure of **5** (50% thermal ellipsoids).

The solid state structure of **5** depicted in Figure 1 is remarkably symmetric with only 1/4 of the molecule being crystallographically independent. The C3–N1 bond length of 1.165(3) Å observed for **5** is typical for an isocyano $\text{N}\equiv\text{C}$ triple bond.⁸ Every carboxylate unit in **5** is essentially coplanar with the azulenic moiety to which it is attached. The long axis of **5** spans 17.1 Å, as defined by the C3...C3' distance. The C6–C6' bond connecting the azulenic rings in **5** is 1.512(4) Å long. This distance is statistically shorter than the $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^3)$ bond of 1.535(4) Å connecting the two seven-membered rings in 1,1',6,6'-tetrahydro-6,6'-biazulene-1,1'-diide, $[\text{H}_8\text{C}_{10}\text{--C}_{10}\text{H}_8]^{2-}$,¹⁵ but only marginally longer than the central C–C bond length documented for biphenyl (1.494(3)–1.507 Å).^{16,17}

The 66.9° torsion angle between the azulenic planes in crystalline **5** is almost certainly significantly influenced by crystal packing forces. Our density functional theory (DFT) analysis of 2,2'-diisocyano-6,6'-biazulenyl (**5a**), a truncated analogue of **5** that lacks all ester substituents, predicts the equilibrium interplanar angle of 52.0° for this model compound with the barriers to internal rotation about the C6–C6' bond to achieve the planar and orthogonal conformations being $\Delta E(0^\circ) = 8.2$ kcal/mol and $\Delta E(90^\circ) = 1.3$ kcal/mol, respectively. Notably, both experimental and recent DFT studies of biphenyl indicate that the $\text{H}_5\text{C}_6\text{--C}_6\text{H}_5$ molecule exhibits the torsional angle of *ca.* 45° with the rotational barriers $\Delta E(0^\circ) \approx \Delta E(90^\circ) \leq 2.0$ kcal/mol in the gas phase.¹⁸ While the $\Delta E(90^\circ)$ values for both **5a** and $(\text{C}_6\text{H}_5)_2$ are similar, the higher $\Delta E(0^\circ)$ value for **5a** reflects greater steric congestion about the central C–C bond connecting the two seven-membered rings in the planar conformation of **5a** compared to the environment of the central C–C linkage in the planar orientation of biphenyl.

Compound **1**, the structure of which may be viewed as one-half of that of **5**, undergoes an irreversible one-electron reduction at $E_{\text{pc}} = -1.55$ V vs $\text{Cp}_2\text{Fe}^+/\text{Cp}_2\text{Fe}$ in CH_2Cl_2 . In sharp contrast, the cyclic voltammogram (CV) of **5** in the same solvent features a nicely reversible ($i_{\text{pc}}/i_{\text{pa}} = 1.0$) two-electron reduction wave at the substantially less negative potential of $E_{1/2} = -1.02$ V (Figure 2). This observation echoes the reduction behavior of the “parent” 6,6'-biazulenyl addressed by Hünig and Ort in a series of their pioneering

redox studies of various biazulenenic motifs.¹⁹ The persistence of 5^{2-} , at least on the electrochemical time scale, can be attributed to the closed-shell nature of its 6,6'-biazulenide dianion framework (Figure 3, left).^{10b,19d,20} The singlet electronic configuration of 5^{2-} is also suggested by our DFT examination of its model **5a**²⁻. The singlet (S) state of **5a**²⁻ is predicted to be nearly 0.7 eV less energetic than the triplet (T) state. The DFT calculations show that the reduction process **5a** → **5a**²⁻ (S) is accompanied by appreciable shortening of the central C–C bond, as well as by a 30° decrease in the interplanar angle between the two azulenic moieties (Table 1). The HOMO of **5a**²⁻ (S) illustrated in Figure 3 clearly implies the significant double bond character of the dianion's central C–C linkage. Similar to **5**, the CV of **3** also features one reversible reduction wave, which occurs at a more negative potential ($E_{1/2} = -1.64$ V) compared to that of **5** due to the electron-donating nature of the $-\text{NH}_2$ termini.

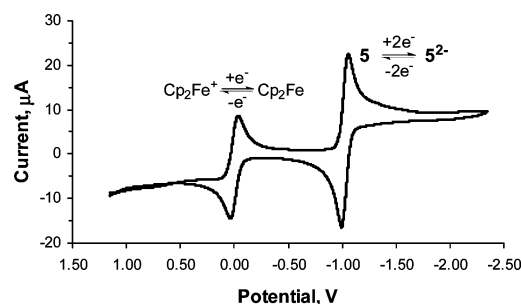


Figure 2. Cyclic voltammogram of **5** in 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]/\text{CH}_2\text{Cl}_2$ vs internal $\text{Cp}_2\text{Fe}^+/\text{Cp}_2\text{Fe}$ (1 equiv) at 25 °C. Scan rate = 100 mV/s.

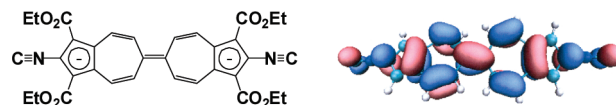


Figure 3. Left: bis(cyclopentadienide)-like resonance form of 5^{2-} . Right: DFT-generated HOMO of **5a**²⁻ (S).

Table 1. DFT-Generated Relative Energies in the Gas Phase (ΔE_{gas}) and in Dichloromethane (ΔE_{DCM}), Interplanar Dihedral Angles (α), and the Central C–C Bond Length (d) for **5a**, **5a**²⁻ (S), and **5a**²⁻ (T)

Model species	ΔE_{gas} , eV	ΔE_{DCM} , eV	α , deg	d , Å
5a	0	0	52.0	1.50
5a ²⁻ (S)	−1.58	−5.92	21.9	1.43
5a ²⁻ (T)	−0.91	−5.23	58.5	1.51

The molecule of **5** can be readily used to bridge metal centers. For example, treatment of *in-situ*-generated $\text{W}(\text{CO})_5(\text{THF})$ with 0.5 equiv of **5** in THF provided fuchsia-colored $[(\text{OC})_5\text{W}]_2(\mu\text{-5})$ that features two “(OC)₅W” units linked through the 6,6'-biazulenyl bridge by means of the $\text{N}\equiv\text{C}$ junctions. Complex $[(\text{OC})_5\text{W}]_2(\mu\text{-5})$ undergoes a reversible reduction at $E_{1/2} = -1.01$ V in CH_2Cl_2 . This reduction potential is almost identical to that of **5** thereby indicating that the LUMO of $[(\text{OC})_5\text{W}]_2(\mu\text{-5})$ is largely bridge-based. The lowest energy band ($\lambda_{\text{max}} = 496$ nm) in the electronic spectrum of $[(\text{OC})_5\text{W}]_2(\mu\text{-5})$ can be assigned to the metal-to-bridge charge transfer (MBCT), and its molar extinction coefficient (ϵ) is *ca.* 35 times greater than that documented for the $S_0 \rightarrow S_1$ transition for **5**. Notably, the analogous MBCT for $[(\text{OC})_5\text{W}]_2(\mu\text{-2,6-diisocyano-1,3-diethoxycarbonylazulene})$ has a λ_{max} value of 515 nm,⁸ whereas the corresponding transition for $[(\text{OC})_5\text{W}]_2(\mu\text{-1,4-diisocyanobenzene})$ occurs in the UV region ($\lambda_{\text{max}} = 370$ nm).²¹

Exposure of a gold-coated mica substrate to a 2 mM solution of **5** in CH_2Cl_2 without protection from air led to adsorption of **5** on

the Au(111) surface. The ellipsometric thickness of the resulting film, measured at multiple spots on the substrate, was 20.5 ± 2.4 Å. This value is consistent with the molecular monolayer nature of the self-assembled film featuring approximately parallel orientation of the long molecular axis of **5** with respect to the surface normal.⁵ Indeed, for the perfectly upright η^1 coordination of **5** to the gold surface (Figure 4), the monolayer thickness can be expected to be approximately 19.1 Å. This estimate is obtained by adding 2.0 Å, a typical Au(0)–CNR bond length,⁵ to the 17.1 Å distance between the two isocyanide carbon atoms in **5** (Figure 1).

The grazing incidence reflection absorption infrared (RAIR) spectrum of a freshly prepared film of **5** on Au(111) also suggests the end-on adsorption of **5** to the Au surface. Indeed, the spectrum exhibits two bands in the isocyanide stretching region (Figure 4). The higher energy band at 2170 cm^{-1} corresponds to $\nu_{\text{C}\equiv\text{N}}$ of the C \equiv N terminus of **5** bound to the gold surface. The broad nature of this band is typical for aryl isocyanide self-assembled monolayers (SAMs) on gold²² and can be attributed to some inhomogeneity in the environment of the surface adsorption sites due to defects in the Au(111) film prepared via gold vapor deposition.²³ Notably, the $\nu_{\text{C}\equiv\text{N}}$ stretch for SAMs of **1** on Au(111) also occurs at 2170 cm^{-1} .⁹ Since the isocyanide carbon's lone pair is antibonding with respect to the C \equiv N bond,¹ donation of electron density from the –NC junction to gold upon chemisorption of **5** results in a pronounced (43 cm^{-1}) blue shift in ν_{CN} for the gold-bonded isocyanide terminus of **5** relative to that of the compound in solution. Concurrently, such coordination should induce a slight positive charge^{7c} within the π -system of **5**, which may lead to weakening of the C \equiv N bond of the unbound isocyanide group, provided there is a sufficient extent of conjugation between the two azulenyl moieties. In accord with this argument, the sharp $\nu_{\text{C}\equiv\text{N}}$ band at 2119 cm^{-1} in the RAIR spectrum in Figure 4 that corresponds to the uncoordinated –N \equiv C end of **5** is depressed by 8 cm^{-1} relative to $\nu_{\text{C}\equiv\text{N}}$ observed for **5** in CH_2Cl_2 solution (or by 11 cm^{-1} compared to $\nu_{\text{C}\equiv\text{N}}$ for the bulk compound in Nujol mull). Interestingly, when adsorbed on metallic gold, linear benzenoid diisocyanoarenes featuring up to three linked arylene units show 2–9 cm^{-1} red shifts in ν_{CN} for their free –N \equiv C end relative to ν_{CN} for the corresponding bulk substances.^{22b,d}

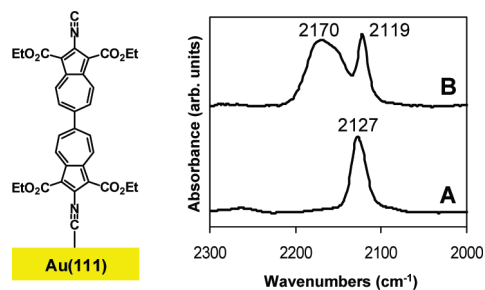


Figure 4. Left: schematic drawing of the terminal upright (η^1) bonding of **5** to the gold surface. Right: $\nu_{\text{C}\equiv\text{N}}$ regions of (A) FTIR spectrum of **5** in CH_2Cl_2 solution and (B) RAIR spectrum of a SAM film of **5** on Au(111).

The SAM of **5** described herein constitutes the first example of a molecular film involving a biazulenyl scaffold. Accessibility of such SAMs presents a hitherto unavailable intriguing opportunity to experimentally probe⁷ the conductivity characteristics of a 6,6'-biazulenyl-based molecular wire. Further studies advancing the coordination and surface chemistry of the 6,6'-biazulenyl and 6,6'-biazulenide frameworks are underway in our laboratory.

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Supporting Information Available: Experimental procedures; spectroscopic and analytical data; details of the electrochemical, X-ray, surface, and DFT studies (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Barybin, M. V. *Coord. Chem. Rev.* **2010**, *254*, 1240–1252.
- (2) (a) Dias, J. R. J. *Phys. Org. Chem.* **2007**, *20*, 395–409. (b) Burdzinski, G.; Kubicki, J.; Maciejewski, A.; Steer, R. P.; Velate, S.; Yeow, E. K. L. *Mol. Supramol. Photochem.* **2006**, *14*, 1–36. (c) van der Veen, M. H.; Rispens, M. T.; Jonkman, H. T.; Hummelen, J. C. *Adv. Funct. Mater.* **2004**, *14*, 215–223. (d) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789–1816. (e) Treboux, G.; Lapstun, P.; Silverbrook, K. J. *Phys. Chem. B* **1998**, *102*, 8978–8980.
- (3) Shevyakov, S. V.; Li, H.; Muthyala, R.; Asato, A. E.; Croney, J. C.; Jameson, D. M.; Liu, R. S. H. *J. Phys. Chem. A* **2003**, *107*, 3295–3299.
- (4) For a class III mixed-valence species, in which the electronic coupling is mediated by the 2,6-azulenedicarboxylate bridge, see: Barybin, M. V.; Chisholm, M. H.; Dalal, N. S.; Holovics, T. H.; Patmore, N. J.; Robinson, R. E.; Zipse, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 15182–15190.
- (5) Lazar, M.; Angelici, R. J. Isocyanide Binding Modes on Metal Surfaces and in Metal Complexes. In *Modern Surface Organometallic Chemistry*; Basset, J.-M.; Psaro, R.; Roberto, D.; Ugo, R., Eds.; Wiley-VCH: Weinheim, 2009; pp 513–556 and references therein.
- (6) Selected recent theoretical reports: (a) Li, Y.; Lu, D.; Galli, G. *J. Chem. Theory Comput.* **2009**, *5*, 881–886. (b) Li, Y.; Lu, D.; Swanson, S. A.; Scott, J. C.; Galli, G. *J. Phys. Chem. C* **2008**, *112*, 6413–6421.
- (7) Representative examples: (a) Choi, S. H.; Kim, B.; Frisbie, C. D. *Science* **2008**, *320*, 1482–1486. (b) Chu, C.; Ayres, J. A.; Stefanescu, D. M.; Walker, B. R.; Gorman, C. B.; Parsons, G. N. *J. Phys. Chem. C* **2007**, *111*, 8080–8085. (c) Kim, B.; Beebe, J. M.; Jun, Y.; Zhu, X.-Y.; Frisbie, C. D. *J. Am. Chem. Soc.* **2006**, *128*, 4970–4971. (d) Murphy, K. L.; Tysoe, W. T.; Bennett, D. W. *Langmuir* **2004**, *20*, 1732–1738. (e) Hong, S.; Reifemberger, R.; Tian, W.; Datta, S.; Henderson, J.; Kubiak, C. P. *Superlattices Microstruct.* **2000**, *28*, 289–303.
- (8) Holovics, T. C.; Robinson, R. E.; Weintrob, E. C.; Toriyama, M.; Lushington, G. H.; Barybin, M. V. *J. Am. Chem. Soc.* **2006**, *128*, 2300–2309.
- (9) DuBose, D. L.; Robinson, R. E.; Holovics, T. C.; Moody, D.; Weintrob, E. C.; Berrie, C. L.; Barybin, M. V. *Langmuir* **2006**, *22*, 4599–4606.
- (10) (a) Ito, S.; Terazono, T.; Kubo, T.; Okujima, T.; Morita, N.; Murafuji, T.; Sugihara, Y.; Fujimori, K.; Kawakami, J.; Tajiri, A. *Tetrahedron* **2004**, *60*, 5357–5366. (b) Ito, S.; Okujima, T.; Morita, N. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1896–1905. (c) Kurotobi, K.; Tabata, H.; Miyauchi, M.; Murafuji, T.; Sugihara, Y. *Synthesis* **2002**, 1013–1016. (d) Morita, T.; Takase, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1144–1152. (e) Hanke, M.; Jutz, C. *Synthesis* **1980**, 31–32.
- (11) The X-ray structure of a diazulenol[2,1-*a*:1,2-*c'*]naphthalene derivative, which formally contains the 1,1'-biazulenyl motif has been reported: Ito, S.; Nomura, A.; Morita, N.; Kabuto, C.; Kobayashi, H.; Maejima, S.; Fujimori, K.; Yasunami, M. *J. Org. Chem.* **2002**, *67*, 7295–7302.
- (12) A small amount of an orange-brown mixture isolated after workup in this control experiment contained 1,3-diethoxycarbonyl-2-aminoazulene (the product of debromination of **2**) as one of the major constituents.
- (13) Representative examples: (a) Nising, C. F.; Schmid, U. K.; Nieger, M.; Bräse, S. *J. Org. Chem.* **2004**, *69*, 6830–6833. (b) Kabalka, G. W.; Yao, M.-L. *Tetrahedron Lett.* **2003**, *44*, 7885–7887.
- (14) For **3**, the $S_0 \rightarrow S_1$ band is likely obscured by the lower energy tail of the substantially more intense $S_0 \rightarrow S_2$ transition at $\lambda_{\text{max}} = 459\text{ nm}$.
- (15) Bock, H.; Arad, C.; Näther, C.; Göbel, I. *Helv. Chim. Acta* **1996**, *79*, 92–100.
- (16) Robertson, G. B. *Nature* **1961**, 593–594.
- (17) Trotter, J. *Acta Crystallogr.* **1961**, *14*, 1135–1140.
- (18) (a) Johansson, M. P.; Olsen, J. *J. Chem. Theory Comput.* **2008**, *4*, 1460–1471. (b) Bastiansen, O.; Samdal, S. *J. Mol. Struct.* **1985**, *128*, 115–125.
- (19) (a) Hünig, S.; Ort, B. *Liebigs Ann. Chem.* **1984**, 1905–1935. (b) Hünig, S.; Ort, B. *Liebigs Ann. Chem.* **1984**, 1936–1951. (c) Hünig, S.; Ort, B.; Hanke, M.; Jutz, C.; Morita, T.; Takase, K.; Fukazawa, Y.; Aoyagi, M.; Ito, S. *Liebigs Ann. Chem.* **1984**, 1952–1958. (d) Hünig, S.; Ort, B. *Liebigs Ann. Chem.* **1984**, 1959–1971.
- (20) Ito, S.; Okujima, T.; Morita, N.; Ohta, K.; Kitamura, T.; Imafuku, K. *J. Am. Chem. Soc.* **2003**, *125*, 1669–1680.
- (21) Grubisha, D. S.; Rommel, J. S.; Lane, T. M.; Tysoe, W. T.; Bennett, D. W. *Inorg. Chem.* **1992**, *31*, 5022–5027.
- (22) (a) Toriyama, M.; Maher, T. R.; Holovics, T. C.; Vanka, K.; Day, V. W.; Berrie, C. L.; Thompson, W. H.; Barybin, M. V. *Inorg. Chem.* **2008**, *47*, 3284–3291. (b) Swanson, S. A.; McClain, R.; Lovejoy, K. S.; Alamdari, N. B.; Hamilton, J. S.; Scott, J. C. *Langmuir* **2005**, *21*, 5034–5039. (c) Stapleton, J. J.; Daniel, T. A.; Uppili, S.; Cabarcos, O. M.; Naciri, J.; Shashidhar, R.; Allara, D. L. *Langmuir* **2005**, *21*, 11061–11070. (d) Henderson, J. I.; Feng, S.; Bein, T.; Kubiak, C. P. *Langmuir* **2000**, *16*, 6183–6187.
- (23) Lazar, M.; Angelici, R. J. *J. Am. Chem. Soc.* **2006**, *128*, 10613–10620.

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