Molecular Absorptions/Absorption Edges (eV)

	AgCl	AgBr	AgI	Order
Molecule	5.12,5.85	4.00,5.04	3.56,4.72	Cl > Br > I
Expanded SC	3.83	3.85	3.76	Cl ≤ Br > I
Bulk SC	3.25	2.68	2.33	Cl > Br > I
SOD Unit Cell Size (Å)	8.8708	8.9109	8.9523	Cl < Br < I

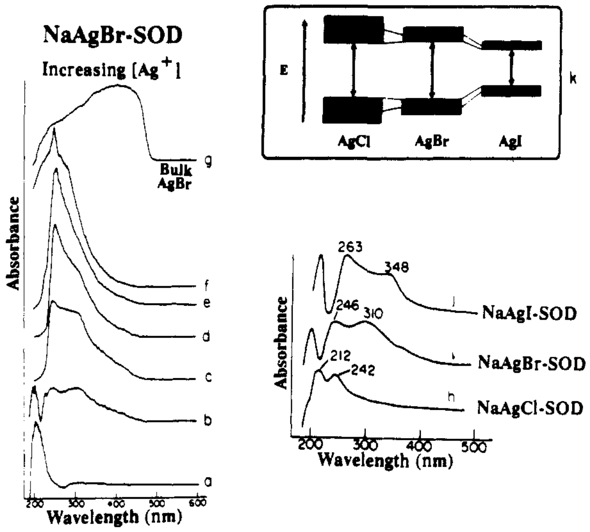

Figure 2. UV–visible reflectance spectra of Na,Ag,Br–sodalites with varying silver concentrations. Ag^+/uc: (a) 0; (b) 0.05; (c) 0.28; (d) 2.0; (e) 3.1; (f) 8.0; (g) bulk AgBr; (h) Na,Ag,Cl–sodalite, 0.1 Ag^+/uc; (i) Na,Ag,Br–sodalite, 0.1 Ag^+/uc; (j) Na,Ag,I–sodalite, 0.1 Ag^+/uc. Note that band-gap absorptions for Na,X-SOD expanded insulators peak at 192 (Cl), 208 (Br), and 214 nm (I) (Figure 2h, i, j) and parallel the order for the bulk fcc NaX materials, 138 (Cl), 165 (Br), and 211 nm (I), respectively.[12] (k) Schematic band diagram for expanded AgX semiconductors.

central anion (4-coordinate $r_{Na^+} = 1.13$ Å, $r_{Ag^+} = 1.14$ Å).[7] At silver concentrations at which most cages contain at least one Ag^+ ion, additional silver results in weakening of the Ag–X bond, preventing further contraction of the unit cell. In the case of Na^+ far-IR absorptions, at lower concentrations the translatory frequency remains essentially constant, but it decreases at higher concentrations when the proportion of cages containing more than one Ag^+ increases. Our present hypothesis is that at low concentrations the AgBr molecules act as isolated defects having no effect on the Na^+ translatory vibrations. Above percolation threshold loadings, the Ag^+ ions must be considered part of the whole unit cell for the vibrational problem, and, because of their weaker interaction with the support compared to sodium, reduce the vibrational frequency of the Na^+ modes.

UV–visible reflectance spectra of Na,Ag,Br–sodalites obtained at various silver loadings show a continuous growth of components at 245–255 and 300–320 nm as the silver concentration increases (Figure 2), corresponding to the $(4d^95s)^1D,^3D \leftarrow (4d^{10})^1S$ excitations of the Ag^+ in $(Na^+)_n(Ag^+)_{4-n}Br$ moieties, respectively. At low Ag^+ loadings, the transitions are similar to the gas-phase values of 230 and 320 nm for the AgBr monomer.[8] In many other host matrices containing quantum-size particles, an increase in the loading of the semiconductor material results in a red shift as the particle size increases.[9] Inside the sodalites, the I–VII cluster nuclearity is limited to five, and no significant absorption (excitation, $\lambda_{em} = 580$ nm) band shifts occur at higher loadings for the Cl^-,Br^- series, in contrast to the I^- series. This difference appears to originate in the more pronounced Ag^+ ion loading sensitivity of the sodalite unit-cell dimensions (inter-β-cage distances and coupling) for the iodide series ($\Delta a_0 = 0.06$ Å) compared to the chloride and bromide series ($\Delta a_0 = 0.02$ Å). Even after complete silver exchange, the absorption edge remains at higher energy than in bulk AgBr. As in the bulk silver halides, the band positions show a halide dependence. A red shift is observed for the bigger anions in larger unit cells in the case of the isolated molecular and fcc bulk[10] forms of the silver halide. The *amonotonic* behavior of the estimated absorption edge[11] for the expanded silver halides is indicative of an interplay of decreasing band gap with decreasing bandwidth down the halide series, implying that the extent of inter-β-cage coupling follows the order of the observed distances between the centers of β-cages, i.e., Cl < Br < I (Figure 2k).

This investigation shows that an organized assembly ranging from isolated molecules to expanded structures stabilized inside a sodalite host matrix can be readily fabricated of a material that is normally a I–VII semiconductor. These materials may be suitable for the chemical synthesis of monodispersed nanostructures, of interest in quantum electronics and nonlinear optics.

Acknowledgment. The financial support of the National Science and Engineering Research Council of Canada (G.A.O., A.S.) and the Office of Naval Research (G.D.S.) is gratefully acknowledged. We thank J. E. MacDougall for helping to collect XRD data.

Supplementary Material Available: Details of the synthesis of sodium–sodalites and silver–sodalites and tables of crystallographic data for NaAgBr–SOD, AgBr–SOD, AgCl–SOD, and AgI–SOD (3 pages). Ordering information is given on any current masthead page.

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Heterosite Reactivity of Linked Bis(μ-phosphido)-Bound Isostructural Co_xMo_{4-x} Clusters (x = 2, 3). Characterization and Reactivity of a Novel μ_4-η^2-NO Cluster[1]

Evan P. Kyba,[*,†] Michael C. Kerby,[*,‡] Ram P. Kashyap,
John A. Mountzouris, and Raymond E. Davis*

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

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Interest in the reactivity of heteronuclear clusters arises from the possibility of site selectivity induced by a particular metal, and novel reactivity patterns via cooperative effects between metal centers.[2] An isostructural array of bimetallic clusters that differ only in their metal–metal ratios might yield insight into the synergistic effects of heteronuclear interactions.[3] In order to study the effects of changing the metal–metal ratio in a series of heteronuclear clusters, we have synthesized and fully characterized a partial family of tetrahedral molybdenum–cobalt clusters that

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[†] Current address: Conner Research Center, Alcon Laboratories, Inc., 6201 South Freeway, Fort Worth, TX 76134.

[‡] Current address: Exxon Research and Development Laboratories, P.O. Box 2226, Baton Rouge, LA 70821.

(1) Linked Bis(μ-phosphido) and Related Ligands for Metallic Clusters. 8. For the preceding paper in this series, see: Kyba, E. P.; Kerby, M. C.; Kashyap, R. P.; Mountzouris, J. A.; Davis, R. E. *Organometallics* **1989**, *9*, 852.

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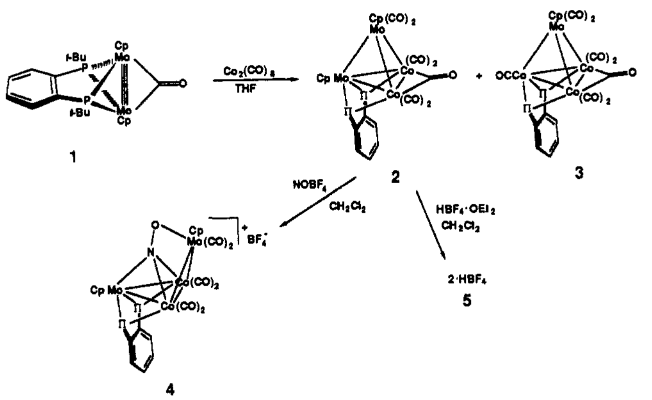
Scheme I[a]



[a] Π = PBu-*t*.

are bound by a linked bis(μ-phosphido)benzene ligand.[4]

We report below dramatic differences in reactivity of two electrophiles, H^+ and NO^+, with two related tetrahedral 1,2-phenylenebis(μ-*tert*-butylphosphido) Co–Mo clusters, Co_xMo_{4-x} [$x = 2$ (**2**), $x = 3$ (**3**)].[4] In particular, we describe the addition of nitrosonium ion to a neutral Mo_2Co_2 cluster, accompanied by the loss of 1 mol of carbon monoxide to give a μ_4-η^2-NO coordination to the Mo_2Co_2 core. Reactions of NO^+ with *neutral* metal clusters to give isolable nitrosyl-ligated clusters are rare.[5]

Clusters **2** and **3** were synthesized under mild conditions via the addition of a linked bis(μ-phosphido)dimolybdenum (Mo≡Mo) complex (**1**)[6] and $Co_2(CO)_8$[7] (Scheme I). The addition of $NOBF_4$ to a CH_2Cl_2 solution of **2** at room temperature for 3.5 h resulted in the loss of CO and the formation of the novel μ_4-η^2-NO-coordinated cluster **4** in 48% yield.[8] Under similar conditions, **3** failed to react with $NOBF_4$ over prolonged periods of time. Addition of excess $HBF_4 \cdot OEt_2$ to a CH_2Cl_2 solution of **2** at 0 °C, followed by warming to room temperature, produced the protonated cluster **5** (14%).[9] No reaction was observed with **3** and $HBF_4 \cdot OEt_2$ under similar reaction conditions.

In both complexes **4** and **5**, NMR spectroscopic studies showed that the molybdenum atoms were different (^1H NMR for Cp: δ (**4**) 5.65 and 5.49; δ (**5**) 5.42 and 4.82), but the phosphorus sites were identical [^1H NMR for *t*-Bu: δ (**4**) 1.72 (d, $J = 18$ Hz); δ (**5**) 1.49 (br s); $^{31}P\{^1H\}$ NMR: δ (**4**) 197 (br s); δ (**5**) 295 (br s); δ (parent cluster **2**) 284 (br s)]. A hydride ^1H NMR signal could not be observed for **5**, even at −80 °C, presumably due to quadrupolar broadening by the ^{59}Co nucleus.[10] Both **4** and **5** were crystalline, but only the former gave crystals suitable for X-ray analysis.

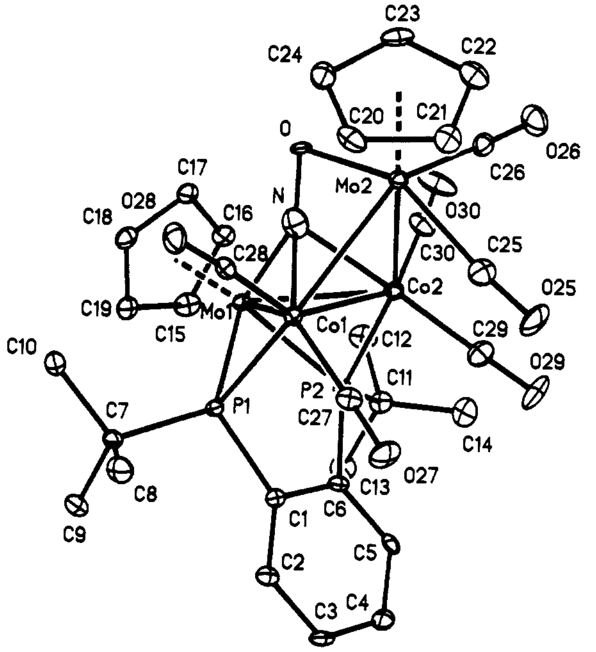


Figure 1. Structure diagram of **4**. Selected bond distances (Å): N–O, 1.27 (7); N–Mo1, 2.014 (6); N–Co1, 1.990 (6); N–Co2, 2.080 (6); O–Mo2, 2.158 (3); Mo1–Co1, 2.6667 (12); Co1–Co2, 2.5358 (14); Co2–Mo1, 2.7006 (12); Co1–Mo2, 2.752 (2); Mo2–Co2, 2.8174 (12); N⋯Mo2, 2.416 (6). Selected bond angles (deg): N–O–Mo2, 85.5 (3); Co1–Mo2–Co2, 54.15 (3); Co1–Mo1–Co2, 56.38 (3); Mo1–N–Co1, 83.5 (2); Mo1–N–Co2, 82.5 (2); Co1–N–Co2, 77.1 (2); Mo1–N–O, 142.7 (4); Co1–N–O, 126.7 (4); Co2–N–O, 121.7 (4). Angle between planes Co1–Mo1–Co2/Co1–Mo2–Co2, 126.2 (1)°.

Examination of the plot of the crystal structure of **4**[11] (Figure 1) shows that cluster **2** has undergone substantial reorganization upon reaction with nitrosonium ion, accompanied by the loss of 1 mol of carbon monoxide. The metal core contains a "butterfly" arrangement of metal atoms, with the two molybdenum atoms as the wing tips and the N–Co1–Co2 array as the central core. None of the metal–metal bond lengths are out of the ordinary.[12] The nitrogen atom of the NO moiety is arranged so as to complete a pseudotetrahedral arrangement with the Mo1–Co1–Co2 plane, and the N–O axis is tipped slightly toward Mo2. The oxygen atom of the bound NO is coordinated to Mo2 (bond length, 2.158 Å) with a Mo2–N–O angle of 85.5°. The O–Mo2 interaction is presumably due to the oxophilicity of molybdenum.[13] The N⋯Mo2 distance (2.416 Å) is too long to be considered a bond. The N–O bond (1.271 Å) is one of the longest reported and consequently should reflect increased reactivity.[14]

To our knowledge, there are no other examples of μ_4-η^2-NO-coordinated clusters, although a few examples of μ_4-η^2-CO-coordinated clusters are known.[15] Tetrahedral → "butterfly"

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(4) Full synthetic details of a series of isostructural phosphido-bound cobalt–molybdenum clusters, Co_xMo_{4-x} [$x = 2$ (2 isomers), 3, 4] are forthcoming: Kyba, E. P.; Kerby, M. C.; Mountzouris, J. A.; Kashyap, R. P.; Davis, R. E. See also ref 1 for spectroscopic and structural details regarding clusters **2** and **3**.

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(7) Higher yields of **3** can be prepared with additional amounts of $Co_2(CO)_8$ at 60 °C. Pure **2** can be converted to **3** with $Co_2(CO)_8$ at 90 °C. A structural isomer of **2** is generated under these conditions.[4]

(8) Cluster **4**: mp >275 °C; ^1H NMR (CD_3CN) δ 7.92 (m, 2 H), 7.15 (m, 2 H), 5.65 (s, 5 H), 5.49 (s, 5 H), 1.72 (d, $J_{P-H} = 18$ Hz, 18 H); ^{31}P NMR δ 197 (br s); IR (CH_2Cl_2) 2047 (s), 2018 (s), 1980 (m, br), 1935 (w, br), 1762 (w, br), 1663 [w, br (ν_{NO})], 1054 [m, br ($\nu_{BF_4^-}$)]; (KBr) 1650 [m, br (ν_{NO})]; MS (CI) 834 ($M^+ - 2CO$, 1), 806 ($M^+ - 3CO$, 100), 778 ($M^+ - 4CO$, 45), 750 ($M^+ - 5CO$, 80). Anal. Calcd for $C_{30}H_{32}O_7P_2Co_2Mo_2BF_4$: C, 36.88; H, 3.30. Found: C, 36.88; H, 3.52.

(9) Cluster **5**: mp >275 °C; ^1H NMR (DMSO-d_6) δ 8.12 (m, 2 H), 7.23 (m, 2 H), 5.42 (s, 5 H), 4.82 (s, 5 H), 1.49 (br s, 18 H); ^{31}P NMR δ (CD_3CN) 295.0 (br s); IR (CH_2Cl_2) 2015 (m), 1985 (s), 1950 (ms, br), 1880 (w, br), 1830 (w, br), 1725 (vw, br) 1025 [s, br ($\nu_{BF_4^-}$)]; MS (CI) 805 ($M^+ - 3CO$, 37), 777 ($M^+ - 4CO$, 19), 749 ($M^+ - 5CO$, 100); molar conductivity (MeCN) = 138 $cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. Calcd for $C_{31}H_{33}O_7P_2Co_2Mo_2BF_4 \cdot 2CH_2Cl_2$: C, 34.59; H, 3.22. Found: C, 35.01; H, 3.32.

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(11) Crystal structure of **4**: at 163 K, space group is $P2_1/n$ (No. 14), $a = 15.614$ (8) Å, $b = 15.992$ (8) Å, $c = 13.965$ (4) Å, $\beta = 103.06$ (2)°, $d_{calcd} = 1.910$ g cm^{-3} for $Z = 4$, $d_{measd} = 1.897$ g cm^{-3} (flotation in aqueous $ZnCl_2$), $F(000) = 1936$. For 5313 unique reflections with $F_o < 4.0\sigma(F_o)$ and 467 variable parameters, the final $R = 0.0471$, $wR = 0.0379$, and goodness of fit = 1.29.

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transformations are typical in cluster reactions with small molecules. Scission of the Mo–Mo bond in the transformation of **2** to **4** is interesting since Mo–Mo bonds are typically thought of as being stronger than Co–Co bonds.[16,17] Electrochemically, **2** exhibits a quasi-reversible oxidative wave at +0.65 V (peak separation, 180 mV) up to +1.0 V. On the other hand, **3** exhibits no oxidation wave up to +0.75 V.[4,18] Reactivity differences observed in this system and, perhaps, those of mixed-metal clusters in general might well be characterized by their redox chemistry.

As part of a study of the chemical properties of cationic cluster **4**, it was treated with hydride nucleophiles. Thus, the addition of 5 equiv of $NaBEt_3H$, $NaBEt_3D$, or $NaB(OMe)_3H$ at −78 °C to **4**, followed by warming to room temperature, regenerated **2** in yields ranging from 65 to 80%. If less than 5 equiv of hydride was used, **2** was only partially regenerated and unreacted **4** was observed by $^{31}P\{^1H\}$ NMR spectroscopy. Possible NO^+ reduction products, NH_3 and H_2O, could not be detected by mass spectrometry. Lithium triethylborodeuteride was used to determine if N–D or O–D products could be observed by ^2H NMR. This technique also proved unsuccessful. It is possible that ammonia was trapped in situ as an amine–borane complex. Not surprisingly, the mechanism of this very interesting transformation is unknown, since in general, hydride reagents react with transition-metal nitrosyl clusters with some complexity.[5,19–21]

In summary, dramatic differences in reactivity are observed between two closely related heteronuclear Mo–Co clusters, **2** and **3**. The addition of NO^+ to **2** involves the scission of the Mo–Mo bond concomitant with CO loss and formation of a novel μ_4-η^2-NO-coordinated cluster. The 1,2-phenylene(bis-μ-phosphido) ligand exhibits stability toward the highly oxidizing nitrosonium ion and appears to prevent fragmentation of the metal core. The novel μ_4-η^2-NO coordination observed in **2** may serve as a useful model for NO activation on heterogeneous surfaces. Further investigations of these bis(μ-phosphido) heteronuclear clusters are in progress.

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Supplementary Material Available: Details of the crystal structure determination and tables of fractional coordinates and isotropic or equivalent isotropic thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, bond lengths and angles, and torsional angles (non-hydrogens) for **4** (15 pages); table of observed and calculated structure factor amplitudes for **4** (36 pages). Ordering information is given on any current masthead page.

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(16) Dissociation energies of homonuclear diatomic molecules $D_0{}^\circ(M_2)$: Co–Co, 40 ± 6 kcal/mol; Mo–Mo, 97 ± 5 kcal/mol; Co–Mo, see ref 2, Chapter 3.

(17) For examples of site-specific M–M bond cleavage in heteronuclear clusters, see: (a) Shapley, J. R.; McAteer, C. H.; Churchill, M. R.; Biondi, L. V. *Organometallics* **1984**, *3*, 1595 (cleavage of a W–W bond was observed as the major product in the reaction of a mixed-metal W_2Ir_2 cluster with C_2Ph_2). (b) Roland, E.; Vahrenkamp, H. *Organometallics* **1983**, *2*, 183 (cleavage of the Co–Co bond in the reaction of a heteronuclear cluster, Co_2Ru_2, with C_2Ph_2).

(18) Cyclic voltammetry was determined with a Bioanalytical Systems BAS-100 (Bioanalytical Systems, West Lafayette, IN) electrochemical analyzer. Acetonitrile solutions of 0.1 M TBAP were used as supporting electrolyte. A Pt disk, Pt wire, and Ag wire were used as the working, auxiliary, and quasi-reference electrodes, respectively. The quasi-reference electrode was calibrated against the Fe/Fe$^+$ couple by addition of ferrocene. (Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1982**, *54*, 1527.) IR compensation was employed in all runs. All manipulations and CV measurements were made under dry argon. Both **2** and **3** exhibit very large irreversible oxidation waves at +1.18 and +0.92 V, respectively. These waves are ascribed to the oxidation of the *o*-phenylene ligand.

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Site-Directed Mutagenesis Reveals That the Hydrophobic Patch of Azurin Mediates Electron Transfer

Mart van de Kamp, René Floris, Frits C. Hali, and
Gerard W. Canters*

Gorlaeus Laboratories, Leiden University
Leiden, The Netherlands

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Despite much recent effort, the experimental support for the various electron transfer (et) mechanisms for blue copper proteins like the azurins and plastocyanins has remained circumstantial.[1–3] Here, for the first time, direct evidence is reported, based on site-directed mutagenesis, which demonstrates the involvement of the so-called hydrophobic patch of *Pseudomonas aeruginosa* azurin in electron transfer. This patch is centered around the partly exposed Cu-ligand residue His117. We have substituted the conserved residue Met44, which is located next to His117, by a lysine. While the structural properties of this mutant azurin fall within the range encompassed by related blue copper proteins, there is a drastic effect on its function in et.

Two places on the protein surface of azurin have been suggested as candidates for exit and/or entry of an electron. The first one is a hydrophobic surface patch located around the Cu ligand His117, which presumably is involved in the reaction of azurin with nitrite reductase[4] and in the electron self-exchange (ese) reaction of azurin.[5,6] A second et patch, formed by an area around His35, might be involved in the reaction with cytochrome c_{551}.[4,7,8] His35 exhibits π-electron overlap with Cu ligand His46. Both His117 and the His35/His46 relay might serve as electronic links between the Cu and the redox partners of azurin. To establish the possible role of the hydrophobic patch in et, we have substituted Met44, a conserved residue[9] located next to His117, by a lysine by means of site-directed mutagenesis.

The presence of the Met44Lys (M44K) mutation shows up in an increase of the p*I* value (wild-type (wt) azurin, 5.6; M44K azurin, 6.6) as measured by isoelectric focusing. Moreover, the Met44 replacement is clearly seen in the ^1H NMR spectrum of the mutant in which the resonance assigned to the ϵ-CH_3 group of Met44 has disappeared[10] (Figure 1).

The effect of the mutation on protein and active-site structure was further investigated by means of EPR, UV/vis, and NMR spectroscopy. The EPR spectra of M44K and wild-type (wt) azurin are shown in Figure 2. Compared to the wt, the $A_\parallel$ and $g_\parallel$ parameters of the mutant have changed from 58×10^{-4} to 64×10^{-4} cm^{-1} and from 2.257 to 2.241, respectively. In the customary D_{2d} model of type I Cu sites,[11] the observed changes in EPR parameters correspond with a change of about 1° in the ligand–Cu–ligand angles, which is within the range encompassed by various wt azurins.[3,12,13]

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* Address correspondence to G. W. Canters, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, The Netherlands.

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