Binuclear sulfide niobium clusters coordinated by diimine ligands: synthesis, structure, photocatalytic activity and optical limiting properties

Alexander V. Rogachev^a, Artem L. Gushchin^{a,b}, Pavel A. Abramov^{a,b}, Ekaterina A. Kozlova,^c Cristian Vicent,^d Dmitry Piryazev,^a Adam Barlow,^e Marek Samoc,^f Mark G. Humphrey^e, Rosa Llusar^d, Vladimir P. Fedin^{a,b} and Maxim N. Sokolov^{a,b*}

Abstract: Substitution reactions of binuclear niobium cluster anion $[\text{Nb}_2\text{S}_4(\text{NCS})_8]^{4-}$ with different types of pyridine-based diimine ligands have been carried out. In the case of 2,2'-bipyridine (bipy) and its derivatives only monosubstituted complexes $[\text{Nb}_2\text{S}_4(\text{NCS})_6\text{L}]^{2-}$ have been isolated. In the case of 1,10-phenanthroline and 2-(2-pyridyl)benzimidazole both mono- and disubstituted complexes, $[\text{Nb}_2\text{S}_4(\text{NCS})_6\text{L}]^{2-}$ and $[\text{Nb}_2\text{S}_4(\text{NCS})_4\text{L}_2]$ respectively, have been obtained. Crystal structures of $(\text{Et}_4\text{N})_2[\text{Nb}_2\text{S}_4(\text{NCS})_6(\text{bipy})] \cdot 0.5\text{bipy} \cdot 0.7\text{CH}_3\text{CN}$ and $[\text{Nb}_2\text{S}_4(\text{pbmz})_2(\text{NCS})_4] \cdot 5\text{DMF} \cdot 0.8\text{H}_2\text{O}$ have been determined. All compounds have been characterized by NMR, ESI mass spectrometry, IR, UV/vis spectroscopies, and CV. $(\text{Et}_4\text{N})_2[\text{Nb}_2\text{S}_4(\text{NCS})_6(\text{bipy})]$ exhibits photocatalytic activity in the reaction of H_2 generation from water in the presence of 0.1 M Na_2S + 0.02 M Na_2SO_3 sacrificial donor system.

KEYWORDS: Chalcogenide clusters, niobium, diimines, crystal structure, NLO properties, HER catalysis.

Introduction

Transition metal complexes of 2,2'-bipyridine and 1,10-phenanthroline and their derivatives display an intriguing combination of structural, electronic and photophysical properties.[1] Relative accessibility of low-lying LUMOs makes these ligands efficient π -acceptors capable of stabilizing metal ions in lower oxidation states. Consequently, metal complexes with these ligands show strong metal-to-ligand charge-transfer (MLCT) absorption bands, often in the visible spectrum, which

may lead to red-shifted fluorescent emissions.[2] Another feature of such ligands is their ability to exist in three different oxidation states, namely, as neutral molecule, as monoanionic radical, and as diamagnetic dianionic species, that is, these ligands can be regarded as non-innocent. An excellent example is provided by the series $[\text{Cr}(\text{bipy})_3]^{3+,2+,1+,0}$ of which all the species contain central Cr^{III} and all the reduction steps are ligand centered.[3] Examples of group 6 complexes featuring N-donor ligands such as $[\text{M}(\text{Mebipy})_3]$ and $[\text{M}(\text{tpy})_2]$ ($\text{M} = \text{Cr}, \text{Mo}$ and W ; $\text{Mebipy} = 4,4'$ -dimethyl-2,2'-bipyridine and $\text{tpy} = 2,2',6',2''$ -terpyridine) have been provided by Wieghardt's group.[4] However, coordination chemistry of such non-innocent ligands with chalcogenide clusters is rather limited, reported examples including coordination of bipyridine or phenanthroline to V_3S_7 ,[5] Mo_3S_4 ,[6] Mo_3Q_7 ($\text{Q} = \text{S}, \text{Se}$),[7] $\text{M}(\mu_3\text{-S})_3\text{Cu}_3$ ($\text{M} = \text{Mo}, \text{W}$)[8] and $\text{Mo}_2\text{S}_2\text{O}_2$ cluster units.[9]

It is expected that "electron sink" properties of the chalcogenide cluster cores coupled with their structural and electronic diversity may lead to novel and potentially important properties. Among the group 5 metals, binuclear clusters of the type $\{\text{Nb}_2(\mu\text{-Q})_2\}^{4+}$ are the best known and stable, including easily available $[\text{Nb}_2(\mu\text{-S})_2(\text{NCS})_8]^{4-}$ complex and its various ligand-substituted derivatives.[10] Theoretical calculations predict that addition of alkenes, alkynes and H_2 across the S_2 ligand to these binuclear clusters might be possible.[11] In this contribution, we report coordination of various pyridine-based diimines, such as 2,2'-bipyridine and 1,10-phenanthroline (Chart 1), to a binuclear $\{\text{Nb}^{\text{IV}}_2(\text{S}_2)_2\}^{4+}$ unit for the first time.

Results and Discussion

Synthesis and characterization

The compounds **2-8** were obtained by refluxing $(\text{Et}_4\text{N})_4[\text{Nb}_2\text{S}_4(\text{NCS})_8]$ or $(\text{Bu}_4\text{N})_4[\text{Nb}_2\text{S}_4(\text{NCS})_8]$ (the latter was used to increase solubility) with bidentate heterocyclic diimine ligands (Chart 1) in acetonitrile. In the case of bipy and its substituted derivatives (dcbpy, dnbbpy), the progress of the substitution was evident from a change in the solution color from the initial orange to deep red (for **2** and **4**) or green (**3**). In all cases, only monosubstituted complexes **2-4** were detected, even if the ligands were employed in excess. The reaction solutions were reduced in volume under vacuum and the crude products were precipitated following addition of diethyl ether. Careful washing with copious amounts of ethanol was necessary to remove unreacted ligand and obtain analytically pure products. We never observed formation of disubstituted uncharged

- [a] Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia
- [b] Novosibirsk State University, Novosibirsk 630090, Russia
- [c] Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia
- [d] Dept. de Química Física i Analítica, Universitat Jaume I, Av. Sos Baynat s/n, 12071 Castelló, Spain
- [e] Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia
- [f] Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, 50-370 Wrocław, Poland
- [g] Serveis Centrals d'Instrumentació Científica, Universitat Jaume I, Av. Sos Baynat s/n, 12071 Castelló, Spain

* author for correspondence: caesar@niic.nsc.ru
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species, which would be insoluble in low- and mid-polarity organic solvents such as dichloromethane.

In the case of the phen and Hpbz, mono-substitution is, however, followed by di-substitution, but the product separation is straightforward since the disubstituted compounds are almost insoluble in acetonitrile and can be isolated by filtration. In the case of Hpbz, dark-red crystals of **7** start to grow on the walls of the reaction vessel even without adding Et₂O. Well-soluble monosubstituted anionic compounds **5** and **8** are then isolated from the acetonitrile mother liquor in the same manner as the bipyridine derivatives.

In contrast to the expectations from the chelate effect, we never observed substitution by more than two bidentate ligands, and in the case of bipyridine derivatives, never more than one. It appears that the bipyridines in solution adopt the *trans*- configuration and closing the chelate cycle requires rotation of a pyridine moiety (see Chart 2). Phenanthroline and 2-(2-pyridyl)benzimidazole do not have this problem because of their rigid geometry and equivalence of both nitrogen atoms in the imidazole cycle in pyridyl-benzimidazole. Upon binding to niobium these ligands do not incur the enthalpic penalty for ring rotation, estimated as 30–35 kJ/mol,[15] and for this reason their complexes tend to be more stable and substitution can proceed further. In contrast, with the bulkier 2,2'-biquinoline, we could not isolate the product of biquinoline coordination to the Nb₂S₄ cluster at all, either by thermal or by photochemical activation. Instead, a co-crystallization product (Hbiquin)₄(Et₄N)₂[Nb₂(μ₂-S₂)₂(NCS)₈](NCS)₂ (**9**) was obtained, in which biquinoline is non-coordinating, and free NCS is present, presumably from a partial destruction of the cluster upon irradiation. The reaction of [Nb₂S₄(NCS)₈]⁴⁻ with another bulky ligand, bichinchonic acid diethyl diester was equally unsuccessful.

The new compounds have been fully characterized by various techniques as described in detail in the experimental section. ¹H and ⁹³Nb NMR spectra support the conclusion that ligand coordination has occurred, and confirm the non-equivalence of the Nb environment in **2** and **3**, respectively. The IR spectra of the compounds show the expected bands for coordinated NCS- (ν(CN) 2060–2100 cm⁻¹ is typical for N-coordinated NCS) and diimine ligands. The S₂ groups afford weak-to-medium IR bands at 580–590 cm⁻¹, the band frequencies being in agreement with those reported previously for the {Nb₂S₄} complexes.[9, 10b]

The ESI mass spectra of the compounds of general formula (R₄N)₂[Nb₂S₄(NCS)₆(diimine)] (**2–5**) display characteristic peaks. The [Nb₂S₄(NCS)₅(diimine)]⁻ anion (formally produced via elimination of a NCS⁻ ligand) is the major peak, and is accompanied by minor signals due to adducts formulated as [Nb₂S₄(NCS)₆(diimine) + R₄N]⁻. For neutral disubstituted compounds, the ESI mass spectra display adducts of general formula [Nb₂S₄(NCS)₄(phen)₂ + NCS]⁻ for phenanthroline, whereas deprotonation of coordinated 2-(2-pyridyl)benzimidazole ligand in [Nb₂S₄(NCS)₄(Hpbz)₂] is the most favorable ionization mode upon ESI(-) conditions, resulting in [Nb₂S₄(NCS)₄(Hpbz)(pbz)]⁻ and [Nb₂S₄(NCS)₄(pbz)₂]²⁻ ions.

All the complexes are intensely colored (ε ≈ 10³ M⁻¹ cm⁻¹) red solids. Monosubstituted complexes **2**, **3**, **5**, and **8** have characteristic maxima in the UV-Vis in the range 360–375 nm,

while disubstitution leads to a substantial bathochromic shift up to 470–475 nm (**6** and **7**). Introduction of the electron-withdrawing carboxylic moiety into dcbpy causes the appearance of a second intense band at 585 nm in the UV-Vis spectrum of **3**, which explains the green color of the complex. No solvatochromic effects have been observed for the complexes. Cyclic voltammetry was performed for compounds **2** and **7** in the presence of 0.05 M Bu₄NPF₆. Both compounds show two irreversible waves at 0.96 V, 1.18 V (**2**) and 0.80 V, 1.30 V (**7**) versus SCE which can be most likely attributed to successive one-electron oxidations at Nb.[16] Irreversible reduction occurs at negative potentials. The crystal structures of compounds **2**·0.5bipy·0.7CH₃CN, **7**·5DMF·0.8H₂O, and **9** have been determined by single-crystal X-ray diffraction techniques.

Crystal structure

The crystal structure of **2**·0.5bipy·0.7CH₃CN consists of the dianion [Nb₂(μ₂-S₂)₂(NCS)₆(bipy)]²⁻ (Figure 1) containing the binuclear cluster core {Nb₂(S₂)₂}⁴⁺ with a single Nb^{IV}-Nb^{IV} bond (d(Nb-Nb) = 2.9171(6) Å), and two μ₂-bridging S₂²⁻ ligands (d(S-S) = 2.009(2), 2.0157(18) Å). The interatomic distances in the {Nb₂(S₂)₂}⁴⁺ core agree well with those found in other Nb₂S₄ complexes.[10a, 17] The niobium atoms in the cluster are not equivalent. Nb1 is coordinated by two NCS⁻ ligands and a bipy molecule, which coordinates in asymmetrical mode [d(Nb-N) 2.276 (4), 2.315 (4) Å]; the shorter bond corresponds to the atom in the equatorial position (roughly coinciding with the plane bisecting both S-S bonds). Nb2 is coordinated by four NCS⁻ ligands in the usual way. The main intracluster distances are summarized in Table 2. In the structure of Cs₄[Nb₂(μ₂-S₂)₂(NCS)₈]·2H₂O the Nb-Nb distances in two crystallographically independent molecules were reported to be 2.8669(15) Å and 2.8580(14) Å,[18] while in (EtQuin)₄[Nb₂(μ₂-S₂)₂(NCS)₈], the Nb-Nb distance is somewhat longer, 2.913(2) Å (EtQuin = N-ethylquinolinium). In the crystal packing the cluster anions form layers orientated in the [110] direction (Figure 2). The space between layers is filled with non-coordinated molecules of bipy and CH₃CN, and the Et₄N⁺ cations. The co-crystallized bipy molecules do not participate in ordered hydrogen bonding, and the nitrogen atoms were placed in the positions consistent with the conformation of the free bipy molecule.

The crystal structure of **7**·5DMF·0.8H₂O is built from neutral molecules [Nb₂(μ₂-S₂)₂(NCS)₄(Hpbz)₂] (Figure 3). The {Nb₂(S₂)₂}⁴⁺ (Table 3) core has the following parameters: d(Nb-Nb) = 2.8924(8) Å, d(Nb-S)_{av} = 2.5055(14) Å, d(S-S) = 2.0143(17) Å. Two Hpbz ligands are coordinated in an anti-fashion relative to the plane comprising the Nb-Nb bond and the midpoints between neighboring unconnected S atoms in the Nb₂S₄ core. The inversion centers of the unit cell are located at the centers of the Nb-Nb bonds. As in **2**·0.5bipy·0.7CH₃CN, the heterocyclic ligand has asymmetrical coordination to the niobium atom, d(Nb-N(py)) = 2.334(4) Å and Nb-N(bz) = 2.234(4) Å, the shorter bond corresponding to the atom in the equatorial position (roughly coinciding with the plane bisecting both S-S bonds). Interactions between the heterocyclic π-systems (3.38–3.42 Å) of the Hpbz ligands produce layers ordered in the [110] direction (Figure 4). The space between the layers is filled with highly disordered DMF and water molecules in such a way that the

independent part of the unit cell has seven positions of DMF molecules with different occupancy factors, the cavity between these positions being occupied by water molecules.

The crystal structure of supramolecular adduct $(\text{Hbiquin})_4(\text{Et}_4\text{N})_2[\text{Nb}_2(\mu_2\text{-S}_2)_2(\text{NCS})_8](\text{NCS})_2$ (**9**) is very complicated. It consists of the $[\text{Nb}_2(\mu_2\text{-S}_2)_2(\text{NCS})_8]^{4-}$ cluster tetraanions, Et_4N^+ cations, uncoordinated NCS^- anions, and monoprotonated Hbiquin^+ cations. The Nb-Nb bonds in the $\{\text{Nb}_2\text{S}_4\}$ units are orientated along the crystallographic b axis, with the Et_4N^+ cations occupying channels that run perpendicular to the Nb-Nb bonds, and aligned with the NCS ligands of $[\text{Nb}_2(\mu_2\text{-S}_2)_2(\text{NCS})_8]^{4-}$ (Figure 5). The bond distances in the cluster tetraanion are listed in Table 4. Such an architecture is probably stabilized by secondary H...S interactions between sulfur atoms of coordinated thiocyanates and the CH_3 groups of Et_4N^+ . The Hbiquin^+ cations form infinite stacks along the crystallographic b axis (Figures 6, 7), the angle between molecules of the adjacent stacks being around 143° . The structure is further supported by π - π interactions within and between the dimers $\{\text{Hbiquin}...\text{Hbiquin}\}_2^{2+}$ (around $3.5 \text{ \AA}$ inside a dimer and around $3.9 \text{ \AA}$ between the dimers). Free NCS^- anions form hydrogen bonds with Hbiquin^+ cations.

Photocatalytic activity

Motivated by strong visible light absorption of the compounds, we have studied the photocatalytic activity of $(\text{Et}_4\text{N})_2[\text{Nb}_2\text{S}_4(\text{NCS})_6(\text{bipy})]$ (**2**) deposited on TiO_2 (type P 25) nanoparticles in the H_2 evolution reaction (HER) from water, in the presence of $0.1 \text{ M Na}_2\text{S} + 0.02 \text{ M Na}_2\text{SO}_3$ as sacrificial donor system, in a setup described previously.[19] The catalytic system under continuous stirring was purged with Ar and irradiated with a high pressure Hg lamp, filtered to allow only wavelengths with $\lambda > 410 \text{ nm}$. The supported photocatalyst containing 5 wt. % of $(\text{Et}_4\text{N})_2[\text{Nb}_2\text{S}_4(\text{NCS})_6(\text{bipy})]$ was prepared by adsorption of the complex dissolved in acetone on TiO_2 under vigorous stirring for 4 h. Before the H_2 evolution experiments, the deposited photocatalyst was dispersed in the aqueous sulfide-sulfite system. Figure 5 demonstrates the dynamics of hydrogen evolution. The rate of the hydrogen evolution was 10 nmol/min or $12 \text{ }\mu\text{mol/g(cat) per hour}$. From the literature, it is known that trinuclear Mo_3S_4 clusters, which are the closest analogues to Nb_2S_4 clusters, efficiently catalyze the evolution of dihydrogen when coupled to a p-type Si semiconductor that harvests red photons in the solar spectrum.[20] It is also known that addition of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ as co-catalyst significantly improves photocatalytic performance of NaTaO_3 in water splitting.[21] Kibsgaard et al. reported that a trinuclear $[\text{Mo}_3\text{S}_{13}]^{2-}$ cluster supported on highly orientated pyrolytic graphite showed extremely high catalytic activity and excellent stability in HER.[22]

Optical limiting properties

The linear and nonlinear optical properties of the complexes with bipyridine ligands (**2-4**) have been examined.[23] Linear optical spectra are displayed in Figure 9 and important spectral data are listed in Table 5. All the studies summarized below were undertaken in DMF. The high-energy bands (λ_1) in the series are comparatively much more intense than the lower-energy bands, and are relatively invariant, spanning the narrow range $306\text{--}312 \text{ nm}$. The lowest-energy λ_3 bands follow the wavelength order **3** >

4 = **2**, complex **3** bearing the electron-withdrawing methyl ester functionality. The UV-visible spectra of **2-4** contain broad low-intensity absorptions through areas of the visible region of the spectrum, suggestive of potential as broad-band optical limiters. Relevant data for optical limiting merit from Z-scan measurements (see Experimental) are collected in Table 5; all clusters absorb weakly at the specific wavelength chosen to assess their optical limiting performance. As we have discussed previously, closed-aperture Z-scan is usually used to derive the nonlinear refractive index n_2 by examining self-focusing or self-defocusing phenomena, while open-aperture Z-scan can afford the nonlinear absorption properties by monitoring the total transmission through a sample;[24] both were employed in the present studies. The closed-aperture scans all show characteristic self-defocusing traces; with the use of relatively long nanosecond laser pulses, the resultant negative refractive nonlinearity may possess contributions from a variety of different mechanisms, including thermal effects, so no further comment is made here. Transmission vs. fluence plots were generated (where the fluence is the energy of the laser pulse per unit area), typical examples (for complex **4**) being shown in Figure 10. For comparative purposes, a threshold limiting fluence $F_{15\%}$ (defined as the incident fluence needed to reduce the transmittance through a sample by 15%) has been used to assess relative optical limiting merit of these clusters, the results being tabulated in Table 1. Assuming a three-state reverse saturable absorption model and employing literature expressions, effective cross-sections of the dominant excited states can be calculated.[25] The energy transmittance of the cell with a Gaussian beam is given by:

$$T = (1 - R)^2 \frac{e^{-\alpha_0 L}}{q} \ln(1 + q)$$

where

$$q = (1 - R)(1 - e^{-\alpha_0 L})\delta_{eff} \frac{F_0}{2F_s}$$

and R is the reflection coefficient, α_0 is the low power absorption coefficient, F_0 is the fluence and F_s is the saturation fluence defined as:

$$F_s = \frac{\hbar\omega}{\sigma_0}$$

and

$$\delta_{eff} = \frac{\sigma_{eff} - \sigma_0}{\sigma_0}$$

Note that these expressions are derived assuming that the lifetime of the state active in the reverse saturable absorption process is longer than the laser pulse duration. Note also that the effective excited-state cross section should only be treated as a measure of the power limiting ability of the substance under specific experimental conditions: it may contain contributions from several different excited states with different properties (e.g. from states of different multiplicity and therefore different lifetimes). The values of the excited-state cross-sections σ_{eff} for **2-4** are given in Table 5. The σ_{eff} values are larger than those of the corresponding ground-state cross-sections σ_0 , which is the condition for the existence of reverse saturable absorption (i.e. all clusters in the present study are optical limiters). The values of σ_{eff} derived in the

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present experiments can in principle be compared to those presented by us before,[24,26,27] but comparisons between values obtained in these different data collection runs should be cautious, since the effective cross-section values are likely to depend to a certain degree on the details of a power limiting experiment such as the pulse duration, the geometric parameters of the laser beam, etc.[28] Comparison between data collected in different laboratories should be even more circumspect. The present σ_{eff} data $4 > 2 > 3$ are suggestive of raising the energy of the ligand π -system (by avoiding incorporation of electron-withdrawing substituents) leading to an improvement in σ_{eff} . While minimizing speculative interpretation, this is consistent with the relevant excited state having significant bipy ligand character, and with tuning of its energy level being a key determinant of optical limiting merit. We are not able to comment further at present; the evaluation of the optical power-limiting mechanism requires time-resolved experiments.

Conclusions

Substitution reactions of the binuclear niobium cluster anion $[\text{Nb}_2\text{S}_4(\text{NCS})_8]^{4-}$ with diimine ligands such as 2,2'-bipyridine (bipy) and its derivatives, 1,10-phenanthroline, and 2-(2-pyridyl)benzimidazole result in mono- and/or disubstituted complexes, $[\text{Nb}_2\text{S}_4(\text{NCS})_6(\text{diimine})]^{2-}$ and $[\text{Nb}_2\text{S}_4(\text{NCS})_4(\text{diimine})_2]$, depending on the nature of the diimine. Crystal structures of $(\text{Et}_4\text{N})_2[\text{Nb}_2\text{S}_4(\text{NCS})_6(\text{bipy})] \cdot 0.5\text{bipy} \cdot 0.7\text{CH}_3\text{CN}$ and $[\text{Nb}_2\text{S}_4(\text{Hpbz})_2(\text{NCS})_4] \cdot 5\text{DMF} \cdot 0.8\text{H}_2\text{O}$ have been established by X-ray structural analyses. All prepared compounds exhibit strong UV-vis absorption. $(\text{Et}_4\text{N})_2[\text{Nb}_2\text{S}_4(\text{NCS})_6(\text{bipy})]$ shows photocatalytic activity in HER in the presence of 0.1 M Na_2S + 0.02 M Na_2SO_3 as sacrificial donor. Though the performance is modest, this results shows that niobium sulfide systems can act as photocatalysts in H_2 evolution. The UV-vis spectra of complexes **2-4** contain broad low-intensity absorptions through parts of the visible region; these complexes function as optical limiters, with the nature of the bipy ligand exerting an influence on optical limiting merit.

Experimental Section

Physical Measurements

Elemental analyses were carried out on a EuroEA3000 Eurovector Analyzer. IR spectra were recorded in the 400–4000 cm^{-1} region on a PerkinElmer System 2000 FT-IR in KBr pellets. Characteristic IR frequencies for the heterocyclic ligands were assigned on the basis of the previously reported complexes.[9] NMR spectra were recorded on a Bruker Avance 500 spectrometer at room temperature. The shifts of the residual protons of the deuterated solvent were used as internal reference. Electronic absorption spectra (200–900 nm) were recorded with a UV/Vis spectrophotometer (Specord M40, Helios γ). A Quattro LC (quadrupole-hexapole-quadrupole) mass spectrometer with an orthogonal Z-spray electrospray interface (Waters, Manchester, UK) was used. Sample solutions were prepared at 1×10^{-5} M in

acetonitrile and typically low cone voltages ($U_c = 20$ V) were used to prevent fragmentation of the identified ions. The chemical composition of each peak in the scan mode was assigned by matching isotopic experimental patterns with those calculated with the MassLynx 4.1 program. Cyclic voltammetry experiments were performed with a 797 VA Computrace electrochemical analyzer (Metrohm, Switzerland). All measurements were carried out with a conventional three-electrode configuration consisting of glassy carbon working and platinum auxiliary electrodes, and a Ag/AgCl reference electrode containing aqueous 3 M KCl. The supporting electrolyte was 0.05 M Bu_4NPF_6 .

General Procedures

All reactions were carried out in air. The starting compound $(\text{Et}_4\text{N})_4[\text{Nb}_2\text{S}_4(\text{NCS})_8]$ was prepared according to the published procedure.[10b] The remaining reagents were obtained from commercial sources and were used as received. NaNCS was dried in vacuum. Solvents for synthesis were dried and deoxygenated by the standard methods prior to use.

The construction of the vibration mill is described in [12]. We used a simplified version of it without a gas outlet. All the operations were carried out in air. A cylindrical titanium reactor was used ($V = 100$ mL, height 50 mm). The reactor was filled with the tungsten carbide-coated steel balls (diameter 10 mm, total mass 320 g) and with a mixture of solid reagents. The reactions were run under the following conditions: reactor vibration frequency 25 Hz, vertical movement amplitude 1 cm, duration of the treatment 2 days.

The NLO experiments were performed on DMF solutions of samples placed in 1 mm glass cells. Linear optical spectra were obtained on a Varian Cary 5 spectrophotometer over the spectral range 270–800 nm, and the light source used for the determination of power limiting properties was an Opolette (HE) 355 II / Opotek system, both being located at the Research School of Chemistry, Australian National University. The Opolette/Opotek is a single-housing tuneable ns laser system in which a flashlamp-pumped frequency-tripled Nd:YAG laser (355 nm pump wavelength, 20 Hz repetition rate, 5 ns pulse length) pumps an optical parametric oscillator (OPO) (tuning range 410–2200 nm, peak OPO energy 10 mJ, spectral linewidth 4–7 cm^{-1}). The optical power limiting experiments were performed on solutions of concentrations 0.20–0.25% w/w. The properties were assessed by the open-aperture Z-scan technique at 600 nm, the specific wavelength being chosen as that at which the samples had low, but non-zero, linear absorption (corresponding to ϵ values of 1140–1920 $\text{M}^{-1} \text{cm}^{-1}$ at the measurement wavelengths). The data from the power limiting curves obtained by the open-aperture Z-scan technique were then converted into transmittance-fluence plots assuming a Gaussian character of the beam, the w_0 parameter of the beam being determined from closed-aperture Z-scan results.

Synthesis of $(\text{Bu}_4\text{N})_4[\text{Nb}_2\text{S}_4(\text{NCS})_8]$ (1**):** A mixture of NbS_2Cl_2 (5.0 g, 22 mmol) and freshly dried NaSCN (7.5 g, 93 mmol) was reacted in the vibration mill [12]. The product was extracted with 300 mL of water and the solution was filtered. Bu_4NBr was then added to the orange filtrate until the precipitation ceased. A copious orange precipitate of **1** was collected by filtration, washed with isopropanol and diethyl ether, and air-dried on the filter. Yield:

35 g (90%). For $C_{72}H_{144}N_{12}Nb_2S_{12}$ calcd: C 49.5; H 8.3; N 9.6; found: C 50.4; H 8.5; N 9.7%. IR (cm^{-1}): 2960 (s), 2934 (s), 2873 (s), 2406 (w), 2294 (w), 2097 (s), 2077 (s), 1728 (w), 1636 (w), 1482 (m), 1470 (m), 1380 (m), 1282 (w), 1152 (w), 1107 (w), 1067 (w), 1029 (w), 960 (w), 924 (w), 882 (w), 799 (w), 736 (w), 583 (w), 530 (w), 479 (w). ^{93}Nb NMR: -548 ppm.

Synthesis of $(Et_4N)_2[Nb_2S_4(NCS)_6(bipy)]$ (2): To a solution of $(Et_4N)_4[Nb_2S_4(NCS)_8]$ (2.00 g, 1.54 mmol) in CH_3CN (50 mL), 2,2'-bipyridine (bipy) (1.00 g, 6.41 mmol) was added. The mixture was refluxed for 12 h. After cooling to room temperature, the red solution was separated from a little amount of a colorless solid by filtration. The volume of the filtrate was reduced by rotary evaporation to 10 mL, and the concentrated solution was diluted with diethyl ether, giving a red precipitate. The solution was kept at 4 °C until the precipitation was complete, and the product was collected by filtration and washed with cold ethanol. Yield: 1.65 g (99 %). Slow diffusion of diethyl ether into an acetonitrile solution of the product yielded red single crystals of $2 \cdot 0.5bipy \cdot 0.7CH_3CN$, suitable for X-ray analysis. For $C_{48}H_{88}N_{10}Nb_2S_{10}$ calcd: C 35.6; H 4.5; N 12.9; found: C 35.4; H 4.4; N 12.7%. IR (cm^{-1}): 2979 (w), 2909 (w), 2072 (vs), 1600 (m), 1471 (m), 1439 (m), 1392 (m), 1312 (w), 1169 (m), 1022 (w), 999 (m), 783 (m), 763 (s), 727 (m), 652 (w), 581 (m), 481 (w). Raman (cm^{-1}): 72 (s), 217 (w), 285 (s), 334 (vs), 420 (w), 446 (w), 470 (w), 590 (m), 634 (m), 653 (w), 844 (m), 921 (w), 1020 (s), 1170 (m), 1261 (w), 1313 (s), 1492 (vs). 1H NMR (CD_3CN): 1.12 (t, 24H), 3.13 (q, 16H), 7.59 (t, 1H), 7.70 (t, 1H), 8.18 (m, 2H), 8.44 (d, 1H), 8.47 (d, 1H), 9.62 (d, 1H), 9.30 (d, 1H). UV-Vis (CH_3CN): $\lambda = 370$ nm, $\epsilon = 3.2 \cdot 10^3$ M $^{-1}$ cm $^{-1}$. ESI(-)-MS (CH_3CN , 20 V) m/z: 759.6 [M - NCS] $^-$. CV (in CH_3CN , vs Ag/AgCl): $E_{pc} = -0.58$, -1.13 , and -1.74 V; $E_{pa} = 0.96$, 1.18 V. Potential route: $1.4 \leftrightarrow -2.2$ V. Scan rate: 0.1 V/s. ^{93}Nb NMR: -613; -280 ppm.

Synthesis of $(Et_4N)_2[Nb_2S_4(NCS)_6(dcbpy)]$ (3): To a solution of $(Et_4N)_4[Nb_2S_4(NCS)_8]$ (0.20 g, 154 μ mol) in CH_3CN (20 mL), di-(4,4'-carboxymethyl)-2,2'-bipyridine (dcbpy) (0.17 g, 685 μ mol) was added. The mixture was refluxed for 16 h under intense stirring. After cooling to room temperature, a dark green solution was filtered from unreacted ligand. The solution was evaporated to dryness and the resultant green-colored product was washed copiously with isopropanol, methanol, and diethyl ether, and then dried in air. Yield: 0.15 g (80 %). For $C_{36}H_{52}N_{10}Nb_2O_4S_{10}$ calcd: C 36.2, H 4.4, N 11.7; found: C 35.6, H 5.0, N 11.6%. IR (cm^{-1}): 2979 (w), 2946 (w), 2072 (vs), 1730 (s), 1617 (w), 1557 (w), 1481 (w), 1437 (m), 1393 (m), 1361 (w), 1326 (w), 1299 (m), 1263 (m), 1225 (w), 1170 (m), 1126 (m), 1066 (w), 998 (m), 958 (w), 783 (m), 761 (m), 718 (w), 697 (w), 581 (m), 481 (w). UV-Vis (CH_3CN): $\lambda = 375$ nm, $\epsilon = 4.7 \cdot 10^3$ M $^{-1}$ cm $^{-1}$; $\lambda = 585$ nm, $\epsilon = 1.5 \cdot 10^3$ M $^{-1}$ cm $^{-1}$. 1H NMR (CD_3CN): 1.24 (t, 24H), 3.21 (q, 16H), 4.03 (d, 6H), 8.06 (d, 1H), 8.20 (d, 1H), 8.92 (d, 1H), 9.01 (d, 2H), 9.58 (d, 1H). ESI(-)-MS (CH_3CN , 20 V) m/z: 875.6 [M - NCS] $^-$; 1063.7 [M + Et_4N] $^+$. ^{93}Nb NMR: -631; -540 ppm.

Synthesis of $(Et_4N)_2[Nb_2S_4(NCS)_6(dnbpy)]$ (4): The compound was prepared as described for **2** from $(Et_4N)_4[Nb_2S_4(NCS)_8]$ (0.20 g, 154 μ mol) and di-(4,4'-nonyl)-2,2'-bipyridine (dnbpy) (0.25 g,

612 μ mol). Yield: 0.11 g (55 %). For $C_{50}H_{84}N_{10}Nb_2S_{10}$ calcd: C 45.1, H 6.4, N 10.5; found: C 45.6, H 6.7, N 10.3%. IR (cm^{-1}): 2903 (s), 2852 (s), 2073 (vs), 1615 (m), 1551 (w), 1483 (m), 1456 (m), 1415 (w), 1393 (w), 1368 (w), 1304 (w), 1284 (w), 1171 (m), 1121 (w), 1000 (m), 834 (w), 784 (m), 721 (w), 581 (m), 482 (w), 423 (w). 1H NMR (CD_3CN): 7.34 (d, 1H), 7.47 (d, 1H), 8.24 (d, 2H), 8.40 (d, 1H), 9.07 (d, 1H). ESI(-)-MS (CH_3CN , 20 V) m/z: 1011.9 [M - NCS] $^-$; 1200 [M + Et_4N] $^+$.

Synthesis of $(Et_4N)_2[Nb_2S_4(NCS)_6(phen)]$ (5) and $[Nb_2S_4(NCS)_4(phen)_2]$ (6): 1,10-phenanthroline (phen) (0.62 g, 3.40 mmol) was added to a solution of $(Et_4N)_4[Nb_2S_4(NCS)_8]$ (0.95 g, 730 μ mol) in CH_3CN (30 mL). The solution was refluxed for 12 h under intense stirring. Cooling the reaction mixture to room temperature afforded a red precipitate that was collected by filtration and then extracted with CH_3CN . The residual solid was dissolved in DMF and diethyl ether was added to the resultant solution, giving a dark-red precipitate of **6** (0.32 g, 40 %). The acetonitrile extract was reduced in volume to 5 mL, diluted with diethyl ether, and cooled, giving a red precipitate of **5**, which was collected by filtration and washed with cold ethanol (0.20 g, 30 %). For $C_{48}H_{88}N_{10}Nb_2S_{10}$ (5) calcd: C 37.0, H 4.4, N 12.7; found: C 37.2, H 4.5, N 12.7. IR (cm^{-1}): 2924 (w), 2058 (vs), 1663 (m), 1518 (m), 1422 (s), 1224 (w), 1145 (w), 1107 (w), 922 (w), 848 (m), 779 (w), 719 (m), 572 (w), 425 (w). 1H NMR (D^6 -DMSO): 1.17 (t), 3.22 (q), 8.10 (q), 8.15 (m), 8.32 (m), 9.08 (m), 9.26 (m), 9.68 (m). UV-Vis (DMF): $\lambda = 360$ nm, $\epsilon = 4.0 \cdot 10^3$ M $^{-1}$ cm $^{-1}$. ESI(-)-MS (CH_3CN , 20 V) m/z: 783.8 [M - NCS] $^-$; 972.0 [M + Et_4N] $^+$. For $C_{28}H_{16}N_8Nb_2S_8$ (6) calcd: C 37.1, H 1.8, N 12.4; found: C 36.9, H 1.9, N 11.7. IR (cm^{-1}): 2061 (vs), 1626 (w), 1581 (w), 1541 (w), 1519 (m), 1495 (w), 1425 (m), 1342 (w), 1224 (w), 1144 (m), 1107 (m), 869 (w), 845 (m), 773 (w), 723 (w), 646 (w), 426 (w). 1H NMR (D^6 -DMSO): 7.94 (m), 8.45 (m), 8.50 (m), 8.70 (d), 9.18 (m). UV-Vis (DMF): $\lambda = 470$ nm, $\epsilon = 5.0 \cdot 10^3$ M $^{-1}$ cm $^{-1}$. ESI(-)-MS (CH_3CN , 20 V) m/z: 964.0 [M + NCS] $^+$.

Synthesis of $[Nb_2S_4(NCS)_4(Hpbz)_2]$ (7): $(Et_4N)_4[Nb_2S_4(NCS)_8]$ (0.20 g, 154 μ mol) was dissolved in CH_3CN (15 mL), and 2-(2-pyridyl)benzimidazole (Hpbz) (0.24 g, 1.23 mmol) was added. The solution was refluxed for 12 h under intense stirring. Cooling the reaction mixture to room temperature produced a red precipitate, which was collected by filtration and washed with CH_3CN . The precipitate was then dissolved in DMF; careful addition of diethyl ether to the solution afforded dark-red crystals of $7 \cdot 5DMF \cdot 0.8H_2O$ suitable for X-ray analysis. Yield: 35 mg (24 %). For $C_{28}H_{18}N_{10}Nb_2S_8$ calcd: C 35.9, H 1.9, N 15.0; found: 35.8, H 1.9, N 14.8. IR (cm^{-1}): 3062 (w), 2922 (w), 2870 (w), 2758 (w), 2653 (w), 2059 (vs), 1649 (s), 1607 (m), 1482 (m), 1455 (m), 1442 (m), 1384 (m), 1325 (w), 1301 (w), 1277 (w), 1253 (w), 1156 (w), 1101 (w), 1066 (w), 1010 (w), 982 (w), 903 (w), 819 (w), 786 (w), 747 (m), 668 (w), 581 (w), 535 (w). UV-Vis (DMF): $\lambda = 475$ nm, $\epsilon = 2.4 \cdot 10^3$ M $^{-1}$ cm $^{-1}$. ESI(-)-MS (CH_3CN , 20 V) m/z: 466.8 [M - 2H] $^{2-}$; 875.8 [M - 2H - NCS] $^-$; 934.8 [M - H] $^-$. CV (in DMSO, vs Ag/AgCl): $E_{pc} = -0.73$, -1.01 , and -1.92 V; $E_{pa} = 0.8$, 1.3 V. Potential route: $1.5 \leftrightarrow -2.3$ V. Scan rate: 0.1 V/s.

Synthesis of $(\text{Bu}_4\text{N})_2[\text{Nb}_2\text{S}_4(\text{NCS})_6(\text{Hpbz})]$ (8**):** $(\text{Bu}_4\text{N})_4[\text{Nb}_2\text{S}_4(\text{NCS})_8]$ (**1**) (0.27 g, 154 μmol) was dissolved in CH_3CN (15 mL), and Hpbz (0.24 g, 1.23 mmol) was added. The solution was refluxed for 12 h under intense stirring. After cooling to room temperature, a red precipitate (a) was collected by filtration and washed with CH_3CN , affording an acetonitrile extract (b). Recrystallization of the precipitate (a) from a DMF/ether mixture yielded **7** as an analytically pure sample. The acetonitrile extract (b) was reduced in volume to 5 mL, and then diluted with diethyl ether and cooled, giving a red precipitate. Washing the crude product with cold ethanol gave **8**. Yield: 85 mg (30 %). For $\text{C}_{50}\text{H}_{81}\text{N}_{11}\text{Nb}_2\text{S}_{10}$ calculated: C 44.7, H 6.1, N 11.5; found C 45.5, H 6.3, N 11.5. IR (cm^{-1}): 3063 (w), 2960 (m), 2931 (w), 2872 (w), 2075 (vs), 1607 (w), 1482 (m), 1457 (m), 1444 (m), 1379 (w), 1151 (w), 1011 (w), 981 (w), 880 (w), 748 (m), 580 (w), 480 (w), 438 (w). ^1H NMR ($\text{D}^6\text{-DMSO}$): 0.94 (t), 1.33 (m), 1.58 (m), 3.17 (m), 7.27 (q), 7.35 (t), 7.55 (m), 7.65 (m), 7.87 (m), 8.30 (m), 8.49 (m), 8.67 (m). UV-Vis (CH_3CN): $\lambda = 310$ nm, $\epsilon = 2.1 \cdot 10^4$ $\text{M}^{-1} \text{cm}^{-1}$; $\lambda = 370$ nm, $\epsilon = 1.3 \cdot 10^4$ $\text{M}^{-1} \text{cm}^{-1}$.

Reaction of $(\text{Et}_4\text{N})_4[\text{Nb}_2\text{S}_4(\text{NCS})_8]$ with 2,2'-biquinoline (biquin): To a solution of $(\text{Et}_4\text{N})_4[\text{Nb}_2\text{S}_4(\text{NCS})_8]$ (0.10 g, 77 μmol) in CH_3CN (15 mL), biquin (0.080 g, 312 μmol) was added. No reaction was observed despite prolonged reflux. The mixture was then UV-irradiated in a quartz tube. After 4 h of irradiation, orange needles of $(\text{Hbiquin})_4(\text{Et}_4\text{N})_2[\text{Nb}_2(\mu_2\text{-S}_2)_2(\text{NCS})_8](\text{NCS})_2$ (**9**) appeared on the tube walls.

Structure Determinations

The diffraction data were collected on a Bruker X8Apex-II CCD diffractometer (for compound **2**-0.5bipy-0.7 CH_3CN and **9** at 296 K) and Bruker Apex Duo (for compound **7**-5DMF-0.8 H_2O at 150 K) with MoK α radiation ($\lambda = 0.71073$ Å) by using ω and ϕ scans of narrow (0.5°) frames. The structures were solved by direct methods and refined by full-matrix least-squares treatment against $|F|^2$ with an anisotropic approximation using the SHELXTL software package.[13] Absorption corrections were applied empirically with the SADABS program.[14] Crystallographic data and refinement details are given in Table 1. Further details may be obtained from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC 993543, 993544, 1001214. Copies of this information may be obtained free of charge from <http://www.ccdc.cam.ac.uk>.

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A series of complexes, $[\text{Nb}_2\text{S}_4(\text{NCS})_6\text{L}]^{2-}$ and $[\text{Nb}_2\text{S}_4(\text{NCS})_4\text{L}_2]$, where L is a bipyridine, phenanthroline or 2-(2-pyridyl)benzimidazole (Hpbz) has been prepared. $(\text{Et}_4\text{N})_2[\text{Nb}_2\text{S}_4(\text{NCS})_6(\text{bipy})]$ exhibits photocatalytic activity for H_2 generation from water in the presence of 0.1 M Na_2S + 0.02 M Na_2SO_3 as a sacrificial donor system. The bipy complexes function as optical limiters to 5 ns pulse length 600 nm incident radiation, with the nature of the bipy ligand exerting an influence on the optical limiting merit.

Alexander V. Rogachev^a, Artem L. Gushchin^{a,b}, Pavel A. Abramov^{a,b}, Ekaterina A. Kozlova,^c Cristian Vicent,^g Dmitry Piryazev,^a Adam Barlow,^e Marek Samoc,^f Mark G. Humphrey^e, Rosa Llusar^d, Vladimir P. Fedin^{a,b}, and Maxim N. Sokolov^{a,b*}

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Title

Chart 1.

Chart 2.

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Figure 1. The molecular structure of the cluster dianion $[\text{Nb}_2(\mu_2\text{-S}_2)_2(\text{NCS})_6(\text{bipy})]^{2-}$ in the crystal structure of $2 \cdot 0.5\text{bipy} \cdot 0.7\text{CH}_3\text{CN}$.

Figure 2. Crystal packing of $2 \cdot 0.5\text{bipy} \cdot 0.7\text{CH}_3\text{CN}$, viewed along the crystallographic b axis. Et_4N^+ cations, bipy and CH_3CN molecules are not shown for clarity.

Figure 3. The molecular structure of the cluster $[\text{Nb}_2(\mu_2\text{-S}_2)_2(\text{NCS})_4(\text{Hpbz})_2]$ in the crystal structure of $7 \cdot 5\text{DMF} \cdot 0.8\text{H}_2\text{O}$.

Figure 4. Crystal packing of $7 \cdot 5\text{DMF} \cdot 0.8\text{H}_2\text{O}$, viewed along the crystallographic a axis. Solvent molecules are not shown for clarity.

Figure 5. Channels along the crystallographic *c* axis occupied by Et₄N⁺ cations.

Figure 6. Orientation of the monoprotonated biquinoline cations in the crystal structure of **9**. **Figure 7.** Monoprotonated biquinoline molecules stack along the crystallographic *b* axis.

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Figure 8. Hydrogen photoproduction kinetic curve under visible light over $(\text{Et}_4\text{N})_2[\text{Nb}_2\text{S}_4(\text{NCS})_6(\text{bipy})]$ (5 wt. %) deposited on TiO_2 P25.

Figure 9. Linear optical spectra for complexes **2** (blue), **3** (red), and **4** (green)

Figure 10. Optical limiting behavior of **4**.

Table 1. Crystallographic data for **2**·0.5bipy·0.7CH₃CN, **7**·5DMF·0.8H₂O and **9**.

	2 ·0.5bipy·0.7CH ₃ CN	7 ·5DMF·0.8H ₂ O	9
Chemical formula	C _{38.40} H _{54.10} N _{11.70} Nb ₂ S ₁₀	C ₄₃ H _{54.60} N ₁₅ Nb ₂ O _{5.80} S ₈	C ₉₈ H ₉₂ N ₂₀ Nb ₂ S ₁₄
<i>M_r</i>	1186.05	1316.71	2184.58
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Orthorhombic, <i>Pbcn</i>
Temperature (K)	296	150	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.3964 (8), 14.5178 (11), 18.9632 (15)	10.3277 (15), 11.6007 (15), 14.595 (3)	26.3601 (3), 14.3990 (2), 26.7549 (4)
α , β , γ (°)	91.584 (4), 94.108 (4), 106.890 (4)	82.170 (4), 75.555 (3), 71.986 (3)	
<i>V</i> (Å ³)	2728.1 (4)	1607.0 (4)	10155.1 (2)
<i>Z</i>	2	1	4
<i>F</i> (000)	1217	674	4504
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.84	0.67	0.57
Crystal size (mm)	0.25 × 0.20 × 0.18	0.20 × 0.16 × 0.13	0.25 × 0.15 × 0.12
Diffractometer	Bruker Nonius X8Apex	Bruker Apex Duo	Bruker Nonius X8Apex
<i>T</i> _{min} , <i>T</i> _{max}	0.817, 0.863	0.879, 0.917	0.871, 0.935
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	36474, 7805, 6017	17145, 9712, 6330	57599, 12591, 6864
<i>R</i> _{int}	0.056	0.042	0.045
Range of <i>h</i> , <i>k</i> , <i>l</i>	-11 ≤ <i>h</i> ≤ 11, -16 ≤ <i>k</i> ≤ 16, -21 ≤ <i>l</i> ≤ 21	-14 ≤ <i>h</i> ≤ 14, -16 ≤ <i>k</i> ≤ 16, -20 ≤ <i>l</i> ≤ 20	-32 ≤ <i>h</i> ≤ 33, -19 ≤ <i>k</i> ≤ 18, -32 ≤ <i>l</i> ≤ 26
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.039, 0.135, 1.13	0.073, 0.241, 1.03	0.041, 0.111, 0.91
No. of reflections, parameters, restraints	7805, 568, 0	9712, 383, 0	12591, 693, 96
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.076P)^2 + 0.7129P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1512P)^2 + 0.1147P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 4.8738P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.81, -0.70	1.87, -1.13	0.30, -0.37

Table 2. Selected geometric parameters (Å) of **2**·0.5bipy·0.7CH₃CN.

Nb1—Nb2	2.9171 (6)	Nb1—S2	2.5248 (13)
Nb1—N11	2.194 (5)	Nb1—S3	2.5055 (13)
Nb1—N12	2.188 (5)	Nb1—S4	2.4957 (14)
Nb1—N31	2.276 (4)	Nb2—S1	2.5177 (13)
Nb1—N32	2.315 (4)	Nb2—S2	2.5454 (14)
Nb2—N21	2.179 (5)	Nb2—S3	2.5252 (14)
Nb2—N22	2.188 (5)	Nb2—S4	2.5115 (14)
Nb2—N23	2.201 (5)	S1—S2	2.0157 (18)
Nb2—N24	2.189 (5)	S3—S4	2.009 (2)
Nb1—S1	2.5015 (13)		

Table 3. Selected geometric parameters (Å) of **7**·5DMF·0.8H₂O.

Nb1-N1	2.149(4)	Nb1-S4	2.4952(12)
Nb1-N2	2.158(4)	Nb1-S3	2.5046(14)
Nb1-N4	2.234(4)	Nb1-S4	2.5117(12)
Nb1N3	2.334(4)	Nb1-S3	2.5137(13)
Nb1-Nb1	2.8924(8)		

Table 4. Selected geometric parameters (Å) of (Hbiquin)₄(Et₄N)₂[Nb₂(μ₂-S₂)₂(NCS)₈](NCS)₂ (**9**).

Nb1-Nb1	2.9220(5)	Nb1-N1	2.186(3)
Nb1-S1	2.5026(8); 2.5252(8)	Nb1-N2	2.196(3)
Nb1-S2	2.5039(8); 2.5052(7)	Nb1-N3	2.190(2)
S1-S2	2.0046(12)	Nb1-N4	2.199(3)

Table 5. Linear Optical and Optical-Limiting Data for **2-4**.

cluster	Optical abs λ, nm (ε, 10 ³ dm ³ mol ⁻¹ cm ⁻¹)				<i>F</i> _{15%} (J cm ⁻²) ^b	Cross section (10 ⁻¹⁸ cm ²)	
	λ ₁ (ε ₁)	λ ₂ (ε ₂)	λ ₃ (ε ₃)	λ _m (ε _m) ^a		Ground state, σ ₀	Excited state, σ _{eff}
2	309 (3.4)	372 (0.8)	465 (0.5)	600 (1750)	0.25	0.6	6.3

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	312	336	558	600			
3	(2.4)	(1.2)	(0.6)	(1920)	0.24	0.7	2.4
	306	369	465	600			
4	(4.1)	(0.7)	(0.4)	(1140)	0.33	0.4	15.3

^a Measurement wavelength in nm (extinction coefficient at the measurement wavelength in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$). ^b $F_{15\%}$ is defined as the incident fluence needed to reduce the transmittance through the sample by 15%.