An In-depth Summary Report on Dr. Frieder Jäkle’s Talk

B-N Units as versatile motifs in the design of innovative molecular and polymetric materials

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Introduction

Dr. Freider Jäkle is a Distinguished Professor at Rutger's University, School of Arts and Sciences Chemistry department. He and his research group are doing work investigating the use of heterogeneous organic connecting subunits to tune or control the properties of organic molecules. The primary subunit his group utilizes a boron-nitrogen (B-N) Lewis pair (LP). Lewis base (LB)/Lewis acid (LA) pairs are ideal for bridging conjugated groups and altering the energy levels in the conjugated system, due to the electron donating nitrogen and the electron deficit organoborane.

Conjugated organic structures are important in such fields as fluorescent dyes, organic sensors, optoelectronic devices, and imaging. By using specific Lewis pairs as a subunit connecting π-conjugated groups the HOMO/LUMO gap of the conjugated system can be adjusted to absorb light at specific wavelengths or to change the properties of the molecule. This can tailor molecules to specific applications. The length and morphology of conjugated systems have been used to reduce the HOMO/LUMO energy gap, and consequently the wavelength a conjugated system absorbs and emits light (if it is fluorescent or phosphorescent).[1] Unfortunately, adding conjugated carbon-carbon links will alter other properties of the compound, such as solubility in water and increased susceptibility to oxidation.[2] Substituting a boron-nitrogen (B-N) unit in a conjugated system reduces a molecule's HOMO/LUMO gap without the need to lengthen the conjugated path. This is of value in the medical field, where solubility is an important consideration in the choice of a therapeutic agent, and where near IR (NIR) radiation is preferable due to its ability to penetrate tissues to a much greater degree than UV or visible light.[3]

Research

Dr. Jäkle's group researched using B-N subgroups with applications in areas such as polymers, transient polymer networks, NIR dyes for photothermal therapy, NIR fluorescence, optical sensors, thermally activated delayed fluorescence, self-sensitized reactivity with endoperoxide formation, singlet oxygen production, and others.

Use of a B-N subunit in polymetric elements alters the properties of a polymer in interesting ways. They researched using B-N LPs as cross-links in transient polymer networks (TPN). By using LAs and LBs pairs in the form of boronic esters, with a range tunable equilibrium constants (K_{eq}), they formed TPNs with adjustable properties. The K_{eq}s of the polymer esters they used ranged six orders of magnitude, as seen in Table1.[4] Randomly distributed along a linear polystyrene backbone, these esters were part of flexible polydimethyl siloxone side-chain bridge connectors.[5]

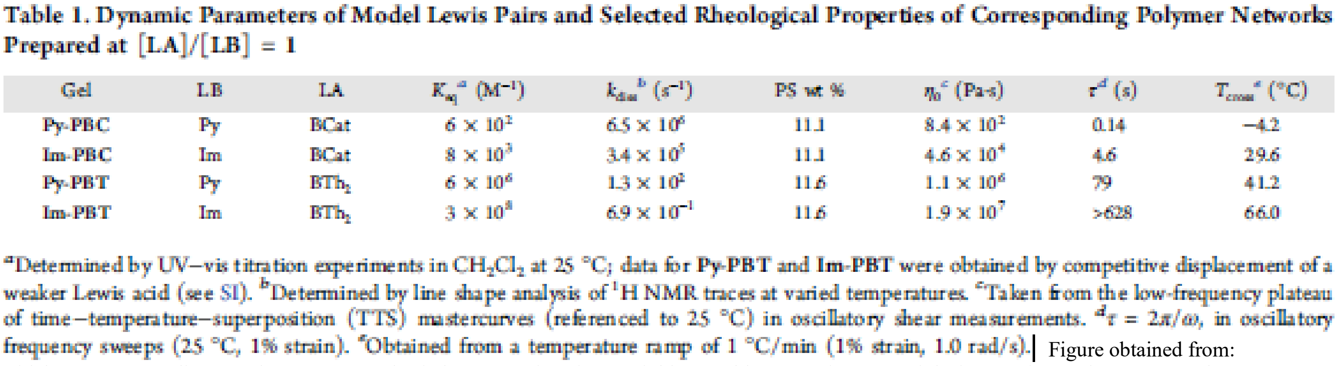

Table 1. Dynamic Parameters of Model Lewis Pairs and Selected Rheological Properties of Corresponding Polymer Networks Prepared at [LA]/[LB] = 1

Gel	LB	LA	K_{eq}[a] (M^{-1})	k_{diss}[b] (s^{-1})	PS wt %	η_0[c] (Pa·s)	τ[d] (s)	T_{cross}[e] (°C)
Py-PBC	Py	BCat	6×10^2	6.5×10^6	11.1	8.4×10^2	0.14	−4.2
Im-PBC	Im	BCat	8×10^3	3.4×10^5	11.1	4.6×10^4	4.6	29.6
Py-PBT	Py	BTh_2	6×10^6	1.3×10^2	11.6	1.1×10^6	79	41.2
Im-PBT	Im	BTh_2	3×10^8	6.9×10^{-1}	11.6	1.9×10^7	>628	66.0

[a] Determined by UV−vis titration experiments in CH_2Cl_2 at 25 °C; data for **Py-PBT** and **Im-PBT** were obtained by competitive displacement of a weaker Lewis acid (see SI). [b] Determined by line shape analysis of ^{1}H NMR traces at varied temperatures. [c] Taken from the low-frequency plateau of time−temperature−superposition (TTS) mastercurves (referenced to 25 °C) in oscillatory shear measurements. [d] $\tau = 2\pi/\omega$, in oscillatory frequency sweeps (25 °C, 1% strain). [e] Obtained from a temperature ramp of 1 °C/min (1% strain, 1.0 rad/s).

Figure obtained from: Vidal, F.; Gomezcoelio, J.; Lalancette, R.; and Frieder, J., Lewis Pairs as Highly Tunable Dynamic Cross-Links in Transient Polymer Networks, Copyright: JACS, 2019

Key: Py – pyridine, Im – imidazole, PBC – pendent catecholboranates, PBT – di(thiophen-yl)boranes

As an additional TPN design element, use of sterically hindered LAs with bulky LBs formed what was referred to as frustrated LPs, in the presence of small molecule gelators, which acted as binding strength modulators. One of the goals was control of the bulk physical properties to form a supramolecular network with reversible non-covalent bonds weak enough to be self-healing at room temperatures. They used tricoordinate boranes as LAs in their TPNs: [4-(tertbutyl) phenyl]catecholboronate and, (4-(tert-butyl)-phenyl)di(thiophen-2-yl)borane]. They used 4-ethyl-pyridine (EtPy) and N-ethyl-imidazole as the LBs.[6] The equilibrium constants of the cross-link esters, formed by the cross-product of the LB/LA components, is found in Table 1.

The Jäkle group worked to develop low band gap chromophores absorbing (and emitting) in the NIR region. Bridging π-conjugation with tricoordinate boron, so the π*-orbitals overlap with the empty p orbitals of the boron to extend the conjugated system, lowering the HOMO/LUMO energy gap. By linking tetracoordinate boron complexes, such as boron formazanates or boron dipyrromethenes, generating conjugated dimers, oligomers, and polymers, they achieved lower energy gaps. The B-N Lewis pair-substituted anthracenes (BDPA) were extended from the monomers to dimer through polymers via vinyl bridges. Several BDPA variations were synthesized, then purified and tested. DFT calculated energy gaps were comparable to those measured via spectroscopic analysis. Fluorescence was measured and for one species, BDPA-Vi2, demonstrated a long lived and intense emission with a quantum yield of 74%. As can be seen in Figure 1, linking monomers increase both emission and absorbance wavelengths, with larger numbers of monomeric units in the molecule. The spectra below is near-IR absorbance and emission of B-N Lewis Pair-Functionalized Anthracenes via selective LUMO extension in conjugated dimer and polymers.

Figure Hidden

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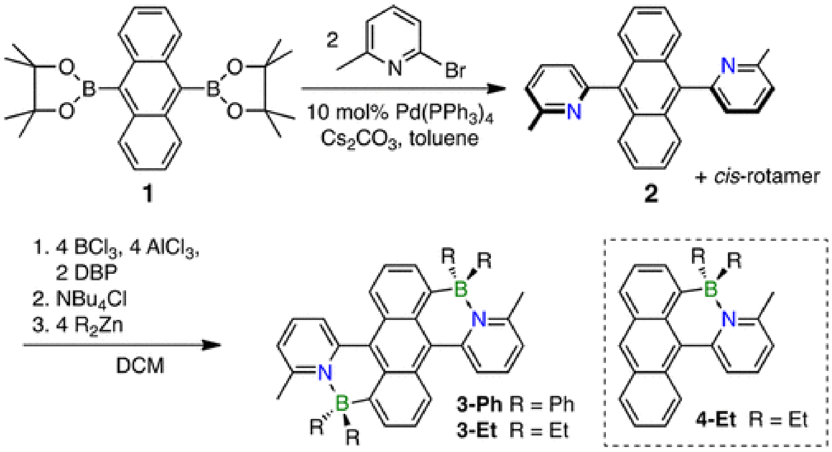
Figure 1 A demonstration of increasing wavelength by increasing the number of monomeric units. Figure obtained from: Zuo.; Liu; Harrell; Fang; Piotrowiak; Shimoyama; Lalancette; Jäkle, Near-IR Emissive B-N Lewis Pair-Functionalized Anthracenes via Selective LUMO Extension in conjugated Dimer and Polymer, Chemie International Edition, 2024, Copyright: John Wiley and Sons, Inc.

Incorporation of B-N subunits into specific polycyclic aromatic hydrocarbons (PAH) caused buckling of the PAH backbone and lowered the LUMO energies. To synthesize them, they reacted 2,2'-(anthracene-9,10-diyl)bis(6-methylpyridine) with BCl_3, $AlCl_3$, and 2,6-di-tert-butylpyridine, then with Bu_4NCl, followed by 4 equivalents of an R_2Zn, in DCM. This yielded three B-N bridged PAHs (Figure 2: 3-Ph, 3-Et, 4-Et) which they analyzed.

^{11}B NMR spectra showed tetracoordinated boron was present in the molecule. Once the three compounds were isolated and crystalized, they utilized X-ray diffraction to analyze the degree of buckling in the molecules. DFT computations (B3LYP hybrid functional with a 6-31g(d) basis set) reproduced the distortions to the backbone seen in the X-ray diffraction studies. X-ray diffraction also allowed the measurement of the bond distances, showing the backbone distortions played a role in, or at least suggested enhanced, π-delocalization. These effects were seen as the reason for the strong bathochromic shift in absorption and fluorescence, compared with an all-carbon analog.

The formed B-N PAH compounds, without the use of external photosensitizer, were seen to quickly react with O_2 in the presence of light, with the reversible formation of their corresponding endoperoxides.[7]



Synthesis of BN-Fused 9,10-Dipyridylanthracenes 3-R (R = Ph, Et) and 4-Et

Figure 2 Synthesis of BDPA compounds. Figure obtained from: Liu, K.; Lalancette, R.; and Jäkle, F., B–N Lewis Pair Functionalization of Anthracene: Structural Dynamics, Optoelectronic Properties, and O_2 Sensitization, Copyright: JACS, 2017

Further research was performed on 9,10-dipyridylanthracenes, attaching methyl groups to the pyridyl groups at the 2, 3, 4, or 5 positions. These structures were designated BDPA-2Me, BDPA-3Me, BDPA-4Me, BDPA-5Me, respectively. DFT computational studies were performed predicting structural energy and structural effects on the molecules, followed by experimental analysis. Kinetic analyses showed BDPA-2Me converted to endoperoxides quickly, with BDPA-5Me converting very slowly, though the BDPA-5Me was an excellent source for singlet oxygen.

Their conclusion was BDPA-2Me had distinct steric interference with the boron-ethyl groups, resulting in a greater B-N bond length (1.690 Å), affecting the reactivity with oxygen. The methyl groups on the pyridyl molecules raised the HOMO and LUMO levels, due to electron donation. They were similar in all positions except position 2 (ortho to N), which raised the energy levels.[8]

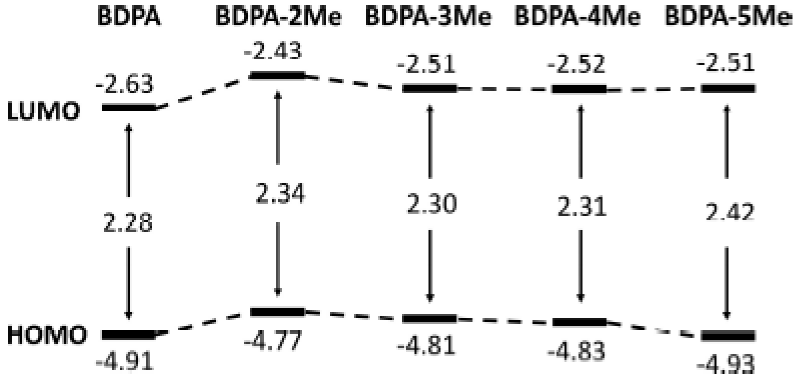


Figure 3 Comparison of HOMO and LUMO energies on BN-acenes. Figure obtained from: Liu, K.; Lalancette, R.; and Jäkle, F., Tuning the Structure and Electronic Properties of B-N Fused Dipyridylanthracene and Implications on the Self-Sensitized Reactivity with Singlet Oxygen, Copyright: JACS, 2019

B-N dative bonds in acenes were investigated with applications as photothermal agents. Dr. Jäkle's group synthesized B-N fused dipyridylanthracenes, using pyrazine linking structure to form a new class of dianthracenylpyrazines with unique electronic properties. See Figure 4, D. By using pyrazine as the electron deficient link with the boron, the LUMO level was dramatically lowered and the HOMO/LUMO gap was quite small (Figure 3). Using C_6F_5, for the R groups on the boron, increased electron deficiency, lowering the gap further. At this point it absorbed in the NIR region. The synthesis used a Pd-catalyzed Suzuki-Miyaura coupling of 9,10-bis (pinacolatoboryl)anthracene with 1-bromo-4-tert-butylbenzene, achieving a 55% yield of 9-(pinacolatobyoryl)-10-(tert-buthylphenyl)anthracene. This was cross-coupled with

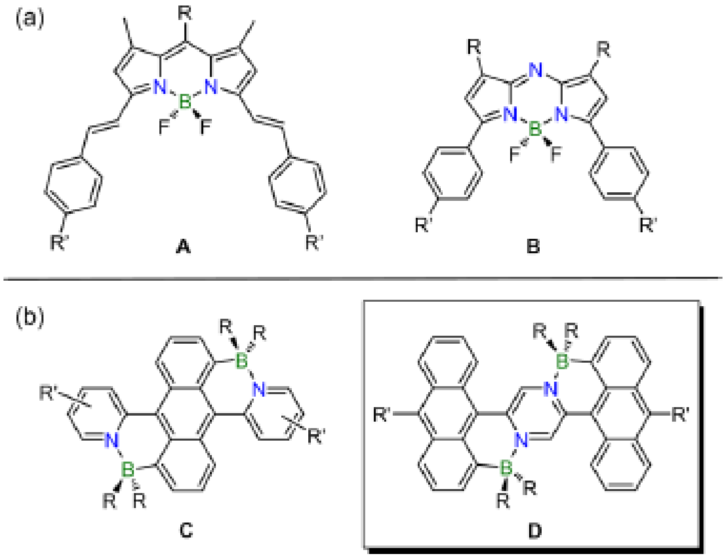


Figure 4. (a) Representative boron complexes applied as photothermal agents and (b) B−N Lewis pair-fused anthracenes as new chromophores. Figure obtained from: Liu, K.; Lalancette, R.; Jiang, Z.; Tang, X.; and Jäkle, F., Near-Infrared-Absorbing B-N Lewis Pair-Functionalized Anthracenes: Electronic Structure Tuning, conformational Isomerism, and Applications in Photothermal Cancer Therapy, Copyright: JACS, 2022

dibromopyrazine producing a pyrazine-bridged anthracene dimer. The addition of BCl_3, $AlCl_3$, and 2,6-di-tert-butylpyridine, in DCM, resulted in an electrophilic borylation. Subsequent reaction with $ZnEt_2$ or $Zn(C_6F_5)_2$ produced the targeted polycyclic acene shown in Figure 4 as D. The fluorinated phenyl version showed higher thermal stability and high photothermal conversion efficiency in the NIR region.[9]

^{11}B-NMR analysis demonstrated expected signals for a tetracoordinated boron configuration. X-ray diffraction of crystals showed a distorted framework connection of the BN-pyrazine-BN bridge between the anthracenes. Figure 5 shows the two conformers of each R group (4-Et for diethyl R groups and 4-Pf for the di(pentafluorophenyl) R groups). This matched DFT computational studies of these molecules [using a B3LYP hybrid functional with a basis set of 31G(d)]. Variable-temperature NMR spectra for the 4-Pf molecule were consistent with rapid

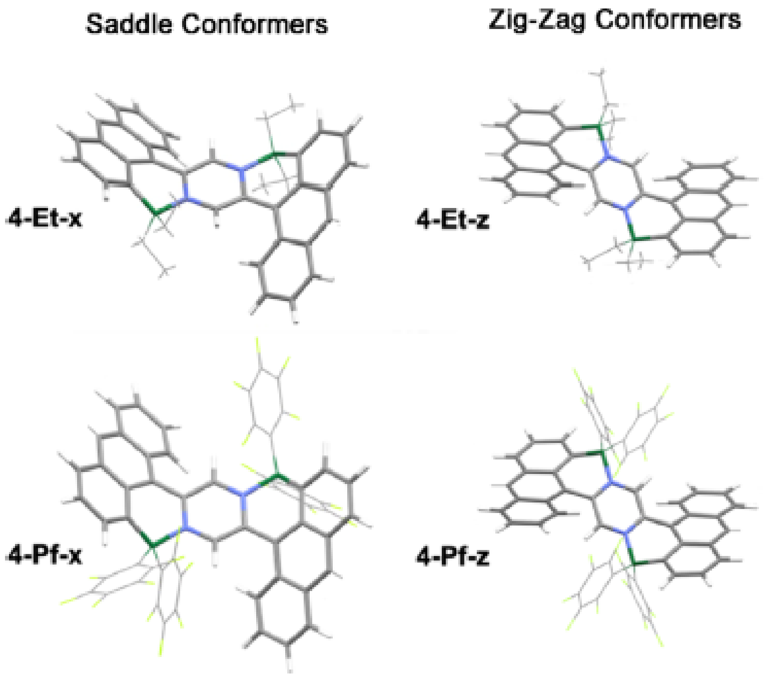


Figure 5. Computed structures of **4-Et** and **4-Pf** (Gaussian 09; RB3LYP/6-31G(d)) illustrating saddle-like conformers (x) and zig-zag conformers (z). C gray, B green, N blue, and F yellow; *tert*-butylphenyl groups omitted for clarity.

Figure obtained from: Liu, K.; Lalancette, R.; Jiang, Z.; Tang, X.; and Jäkle, F., Near-Infrared-Absorbing B-N Lewis Pair-Functionalized Anthracenes: Electronic Structure Tuning, conformational Isomerism, and Applications in Photothermal Cancer Therapy, Copyright: JACS, 2022 interconversions between the 4-Pf-x and 4-Pf-z conformers. UV-vis-NIR absorption spectra showed the 4-Pf molecule with a poor absorption in the visible range but a pronounced absorption peaking at 774 nm. Using TD-DFT analyses (PBE0 hybrid functional with 311g* basis set), they produced results consistent with the observed IR absorption spectrum.[10]

Water-soluble nanoparticles were produced via nanoprecipitation with an amphiphilic copolymer as an agent encapsulating 4-Pf as nanoparticles (4-Pf-Nps). Investigating the 4-Pf-Np photothermal characteristics, in vitro, the nanoparticles were dispersed in water and irradiated with 808 nm light, at a power density of 1 W cm^{-2}. This testing obtained a peak value of 62.8° C, achieved within 10 minutes.[11]

Biocompatibility studies showed a high cell viability at more than 95%. In-vivo tumor studies were used to determine the viability of 4-Pf-Nps as a photothermal therapy (PTT) agent. The PTT efficacy was studied, with respect to tumor growth in mice, for 14 days post PTT treatment. Four groups of four mice each were tested. One group formed a pure control, another treated only with light, one group treated only with 4-Pf-Nps, and an experimental group with light and 4-Pf-Nps. The first three groups (controls) showed negligible therapeutic benefit, with an average 6-fold increase in tumor size. The 4-Pf-Nps with light treatment group showed high anti-tumor efficacy, with the tumors totally eradicated and no recurrence.[12]

Conclusions

Dr. Jäkle and his group have used B-N subgroups as a central design element to tailor properties of materials, such as absorption and emission, reactivity with oxygen, endoperoxides using B-N pair-functionalized acenes, NIR emissive materials to produce photothermal properties with cancer treatment applications, polymer properties that could lead to self-healing plastics, and polymer units that, when linked together, allow adjustment of absorptivity and emissivity based on the number of polymer units incorporated.

Their use of the B-N Lewis pair has widened a field of research allowing tuning of properties with a wide variety of applications. They have delved into the field analyzing the produced materials via computational methodologies, H, ^{13}C, and ^{11}B NMR, X-ray diffraction, not to mention UV/Vis/IR spectroscopy, examining the mechanisms behind material properties observed. Their work is constructing a design scaffold method for targeting desired properties in synthesized compounds/materials, reducing the hit or miss methods of the past.

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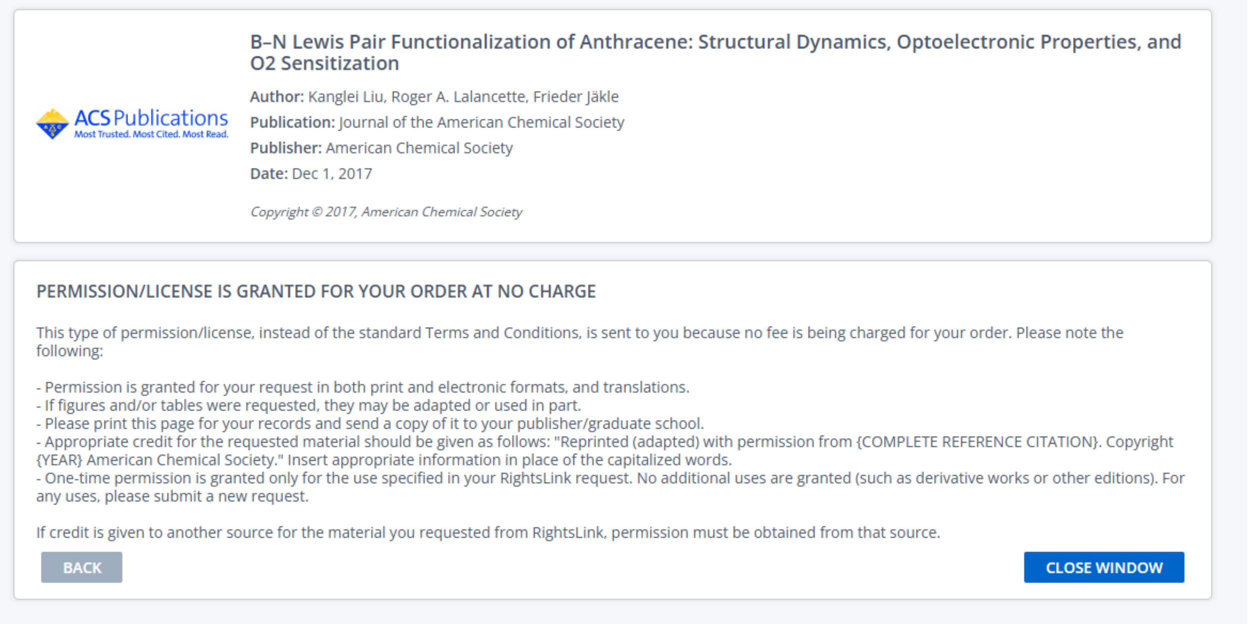

B–N Lewis Pair Functionalization of Anthracene: Structural Dynamics, Optoelectronic Properties, and O2 Sensitization

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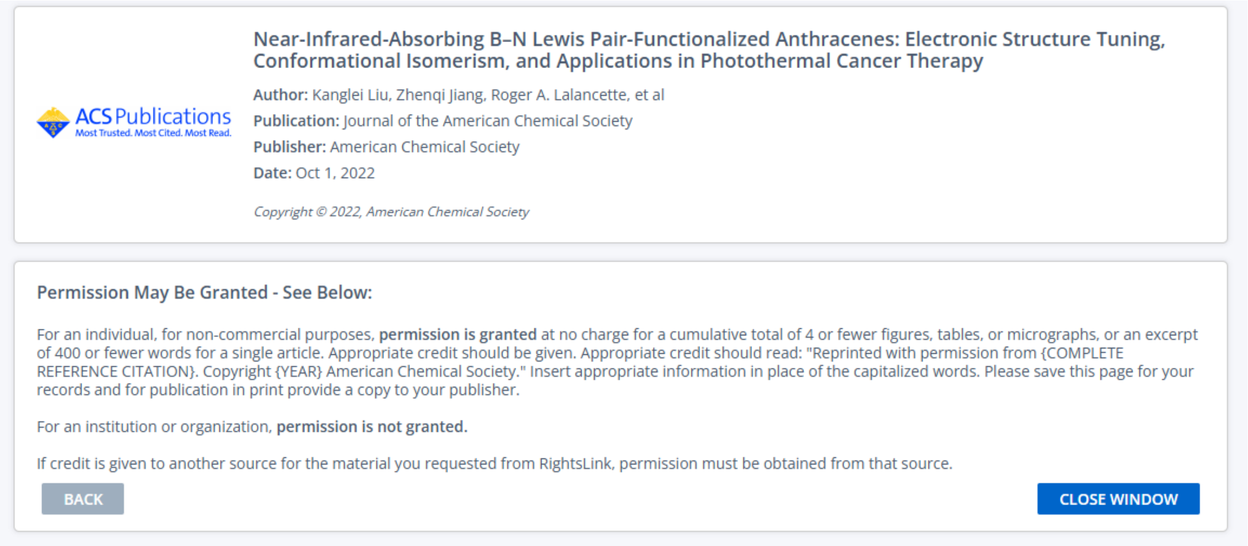

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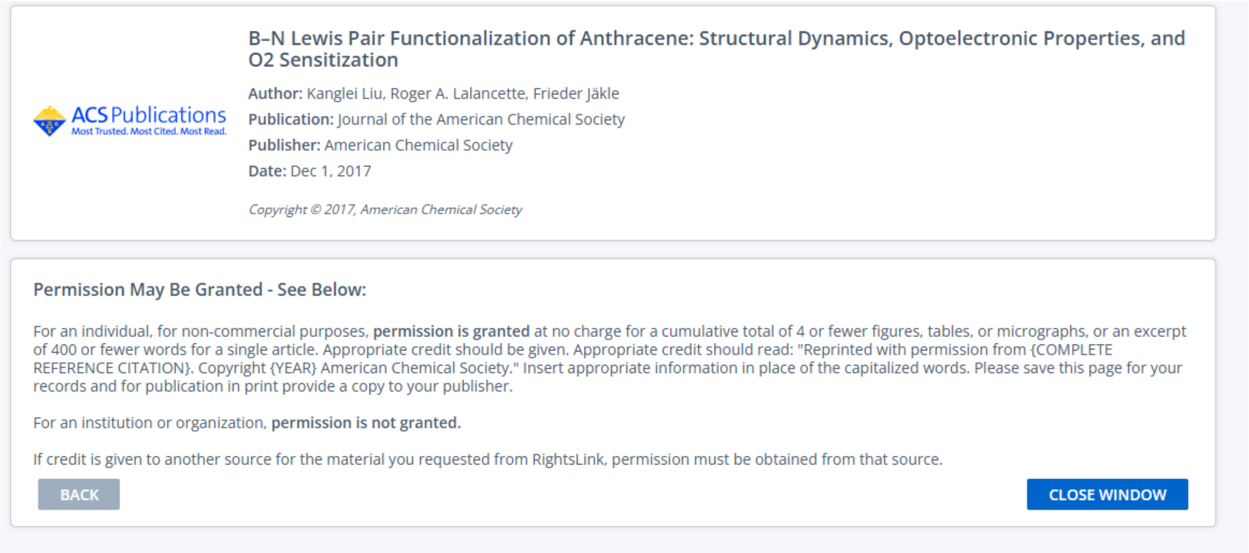

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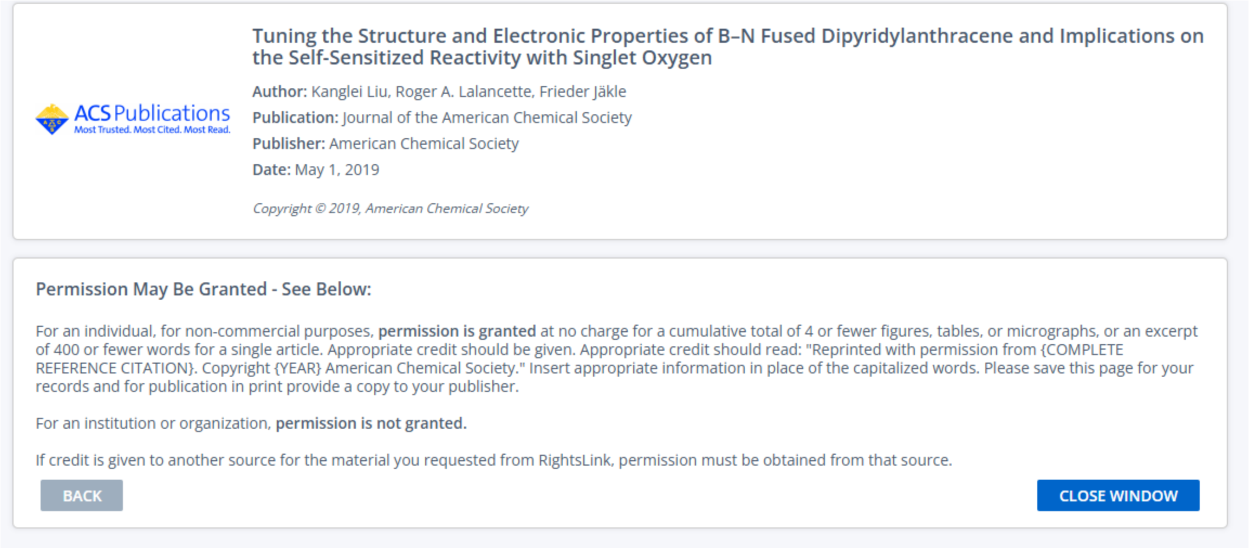

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