

PROGRAM of the RTG-PCL Winter School 2025 at Kurhotel Bad Staffelstein

(<https://www.kurhotel-staffelstein.de/tagung.html>)

Date/ Time	Monday, Nov 03	Tuesday, Nov 04	Wednesday, Nov 05	Thursday, Nov 06	Friday, Nov 07
08:30		Mounting of posters (1 st cohort)			
09:00		Poster flash 1	Poster flash 2	GA meeting (1.5 h)	PI meeting for planning the 2 nd funding period (1 h)
09:30		Poster session 1 (1.5 h)	Poster session 2 (1.5 h)		Coffee break (30 min)
10:00					
10:30					
11:00		Coffee break (30 min)	Coffee break (30 min)	Session on Open Book (1.5 h)	Coffee break (30 min)
11:30		Poster session 1 (1.5 h)	Poster session 2 (1.5 h)		Lunch (hotel) (1.5 h)
12:00					
12:30		Lunch (hotel), Welcome coffee & Registration	Lunch (hotel) (1.5 h)	Lunch (hotel) (1.5 h)	C2: D. Golze
13:00					
13:30					
14:00					
14:30	Opening remarks (1 h)	A5: H.-P. Steinrück	B1: M. Halik	C3: D. Guldi	
15:00		A4: S. Kaskel	B2: T. Heine	C4: J. Maultzsch	
15:30	Coffee break (30 min)	Coffee break (30 min)	Coffee break (30 min)		
16:00	Coffee break (30 min)	A3: F. Hauke	B3: S. Maier	C5: I. Weidinger	
16:30	Flash presentations 2 nd cohort (1 h)	A1: W. Niu	B4: H. Weber	A2: X. Feng	
17:00		C1: E. Brunner	Round-table "Equal Opportunities" (1 h)		
17:30					
18:00	Dinner (hotel) (1.5 h)				
18:30					
19:00					

Further details:

- 2nd cohort DR flash presentations (Monday, 03.11.): Brief personal (+ background) introduction plus short intro to the own RTG-PCL project
- Flash- + Poster-sessions for the 1st cohort (Tue - Wed): Latest results / Progress since last Summer School. Associated DRs are also welcome to participate.
- PI talks (Tue - Thu): (Most prominent) topical developments in the respective running project, including also the overall idea/work plan of the starting 2nd-cohort topic. Highlights of publications stemming from the RTG-PCL, in particular, those co-authored by the doctoral researcher and/or in collaboration with RTG-PCL partners, are welcome to be included. The respective time slots are scheduled for 20 min talk + 10 min for questions and discussions.
- General Assembly (GA) meeting (Thursday, 06.11.): RTG-related topics, incl. status of 1st cohort projects and finalizing the PhD theses, joint publications, publications with DRs as co-authors, development of new courses for the RTG, scheduling the next joint meetings (on-site + summer school), etc.
- Open Book session (Thursday, 06.11.): All PIs and DRs to discuss latest status and development
- Progress meetings DRs + (Co-)Supervisors (Friday, 07.11.): include also feedback on annual written reports (1st cohort), presentations, manuscript drafts, etc. from the supervisor and co-supervisor (if not done earlier or during the school),
- There should be opportunities for the 2nd cohort DRs to meet all PIs and select a mentor!
- We should discuss whether a hobby project competition will take place for the 2nd cohort (Could be during the GA meeting on Thursday and later together with the DRs)

Synthesis of Heptagon-containing Nanographenes & Curved Graphene Nanoribbons

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Nonbenzenoid nanographenes (NGs), characterized by the incorporation of non-hexagonal rings, have garnered significant attention due to their unique topologies and exceptional physicochemical properties, positioning them as promising candidates for optoelectronic and spintronic applications. While pentagons induce positive curvature, heptagons and octagons generate concave, negatively curved structures. Among these, saddle-shaped NGs with heptagonal rings are pivotal for the development of three-dimensional carbon nanostructures such as *schwarzite*, which is predicted to exhibit remarkable electronic and magnetic properties. However, the synthesis of these NGs remains challenging due to the high-strain energies inherent in their highly twisted structures and the lack of efficient synthetic methods for heptagon incorporation.^{1,2}

In addition to the non-benzenoid NGs, curved GNRs (cGNRs) are gaining much attention these days. Capitalizing on their unconventional edge configurations, cGNRs demonstrably exhibit a significantly reduced band gap and superior charge carrier mobility compared to their planar counterparts of comparable widths. Furthermore, cGNRs possessing out-of-plane distortions present intriguing possibilities in the realms of nonlinear optics and asymmetric catalysis. However, the synthetic landscape for cGNRs remains relatively unexplored due to robust synthetic methodologies and the challenge of designing suitable molecular precursors.^{3,4}

This first research introduces a novel synthetic methodology for the construction of heptagon-containing NGs, which has been successfully used to synthesize a saddle-shaped nanographene (SNG), the initial results of which were reported previously.⁵ As an extension of the SNG concept, we now propose two related structures: the heptagon-containing carbon nanoring (hCNR) and the double saddle-shaped nanographene (DNG).

A secondary objective of this work involves the synthesis GNRs, functionalized by the incorporation of a [6]helicene subunit along the ribbon periphery. The presence of this inherently optically active fragment is strongly hypothesized to give rise well-defined molecular chirality to the overall structure. Such chiral architectures are expected to facilitate the exploration of novel optoelectronic and spintronic properties, particularly phenomena such as the Chirality-Induced Spin Selectivity (CISS) effect.

References

- (1) Pun, S. H.; Miao, Q. Toward Negatively Curved Carbons. *Acc. Chem. Res.* **2018**, *51* (7), 1630–1642. <https://doi.org/10.1021/acs.accounts.8b00140>.
- (2) Cheung, K. M.; Xiong, Y.; Pun, S. H.; Zhuo, X.; Gong, Q.; Zeng, X.; Su, S.; Miao, Q. Negatively Curved Molecular Nanocarbons Containing Multiple Heptagons Are Enabled by the Scholl Reactions of Macrocyclic Precursors. *Chem.* **2023**, *9* (10), 2855–2868. <https://doi.org/10.1016/j.chempr.2023.05.028>.
- (3) Narita, A.; Feng, X.; Müllen, K. Bottom-Up Synthesis of Chemically Precise Graphene Nanoribbons: Bottom-Up Synthesis of Chemically Precise Graphene Nanoribbons. *The Chemical Record* **2015**, *15* (1), 295–309. <https://doi.org/10.1002/tcr.201402082>.
- (4) Niu, W.; Ma, J.; Feng, X. Precise Structural Regulation and Band-Gap Engineering of Curved Graphene Nanoribbons. *Acc. Chem. Res.* **2022**, *55* (23), 3322–3333. <https://doi.org/10.1021/acs.accounts.2c00550>.
- (5) Borisov, B.; Beneventi, G. M.; Fu, Y.; Qiu, Z.; Komber, H.; Deng, Q.; Greißel, P. M.; Cadranel, A.; Guldi, D. M.; Ma, J.; Feng, X. Deep-Saddle-Shaped Nanographene Induced by Four Heptagons: Efficient Synthesis and Properties. *J. Am. Chem. Soc.* **2024**, *146* (40), 27335–27344. <https://doi.org/10.1021/jacs.4c09224>.

Length-Dependent Optoelectronic Behavior in Nanographenes

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Molecular nanographenes are emerging as promising materials for optoelectronic and energy-related applications owing to their unique and tunable optical and electrochemical properties.^[1] While significant advances have been in the synthesis of atomically precise nanographenes, a comprehensive understanding of their photophysical and electrochemical behavior is still in its early stages.^[2] In this work, we present a systematic photophysical investigation of a series of molecular nanographenes with varying lengths.^[3,4] Furthermore, we explore their interactions with porphyrins and study their behavior in the aggregated state using a broad range of ultrafast spectroscopic techniques.

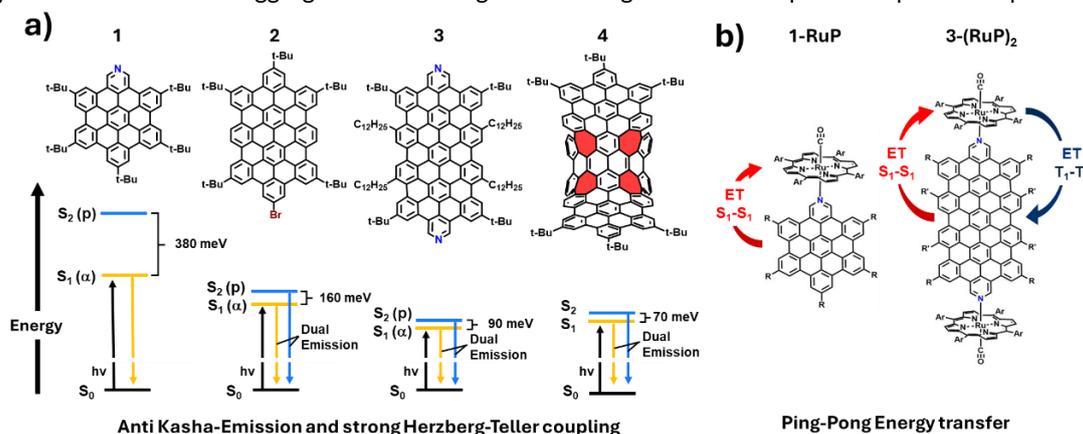


Figure 1. a) Chemical structure of molecular nanographenes with different lengths, and relative energy scheme with the energy of S_1 and S_2 , leading to anti-Kasha emission and Herzberg–Teller vibronic couplings. b) Chemical structure of nanographene-porphyrin hybrids and their length-dependent excited-state deactivation.

Interestingly, we found that increasing the nanographene length results in an energetic proximity between the S_1 and S_2 states, giving rise to rarely observed anti-Kasha fluorescence in **3**. This is accompanied by strong vibronic coupling, which leads to deviations from the widely used Franck–Condon approximation, in favor of Herzberg–Teller activities in **2** and **4**. The nanographene length also influences the excited-state deactivation pathways in their porphyrin (**RuP**) hybrids, as revealed by ultrafast transient absorption spectroscopy. Notably, the hybrid **3-(RuP)₂** exhibits a “ping-pong” energy transfer mechanism, where energy is transferred from the nanographene to the porphyrin and then back again—unlike **1-RuP**, where energy transfer occurs unidirectionally from the nanographene to RuP.

Furthermore, the self-assembly behavior of compounds **2** and **3** in solution was examined in detail, revealing the formation of dimers, followed by two-dimensional supramolecular polymers. Exciton and charge carrier dynamics within these structures were probed using transient emission microscopy and ultrafast terahertz (THz) spectroscopy. Our findings provide a deeper understanding of the optoelectronic properties of nanographenes and underscore the potential of such assemblies for applications in organic electronics, including solar cells and field-effect transistors (OFETs).

References

- [1] Z. Liu, S. Fu, et al. *Adv. Sci.* **2022**, 9, 2106055.
 [2] G. M. Beneventi, M. Krug et al., *J. Photochem. Photobiol. C: Photochem. Rev.* **2023**, 56, 100602.
 [3] G. M. Beneventi, J. Scholl et al., *Adv. Energy Mater.* **2024**, 14, 2401529.
 [4] B. Borisov, G. M. Beneventi et al., *J. Am. Chem. Soc.* **2024**, 146, 27335–27344.

Raman Spectroscopic Characterisation of Graphene Nanoribbons

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Graphene nanoribbons (GNRs) are one-dimensional strips of graphene whose electronic and optical properties can be modified by altering their width, edge structure, and chemical functionalisation. Unlike pristine graphene, GNRs can exhibit semiconducting behaviour with tunable band gaps, making them promising candidates for next generation of nanoelectronic and optoelectronic devices.

This study employs Raman spectroscopy to establish the characteristic vibrational fingerprints of various types of GNRs, including commercially available 4-zigzag GNRs, chemical vapour deposition (CVD)-grown 5-armchair GNRs, and novel cyclophane-shielded GNRs [1]. The current work focuses on preparing and characterising GNR powder samples, polymer-wrapped thin films and mechanically exfoliated GNR layers. Raman measurements are performed with varying excitation energies and laser powers to assess spectral stability and resistance to laser-induced damage. Plans for evaluating the GNR response to perturbations induced by strain and electric fields are also presented.

This work aims to improve the fundamental understanding of the vibrational and optical properties of GNRs, and to clarify how external perturbations, such as mechanical strain and electric fields, affect their vibrational and electronic behaviour. This is an essential step towards their controlled integration into nanoscale devices.

References

[1]J.-J. Zhang et al., Singly Dispersed Graphene Nanoribbons Enabled by Cyclophane-based Shielding Strategy, submitted 2025

Tailoring interfaces – molecular doping of transition metal dichalcogenide nanosheet networks

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Exfoliated 2D transition metal dichalcogenide (TMD) flakes, which self-assemble at liquid-liquid interfaces by means of the Langmuir-Schäfer approach, afford semiconducting nanosheet networks¹ (NN) with properties resembling those in dispersion. In this work, we functionalized NNs of TMDs using phthalocyanines of variable electron donating/accepting strength² en-route towards heterojunctions. In the electronically ground-state an interfacial charge transfer (ICT) evolves that is best described as either n- or p-doped NNs. In the excited, these ICT systems undergo interfacial charge separation (ICS). Decisive insight came from transient absorption measurements, which demonstrated that the direction of ICS is determined by the energy alignment of the molecular orbitals and the TMD bands. Our approach serves as a versatile platform to design interfaces though, for general, interchanging the metal center and/or substituents on the phthalocyanines.

References

- [1] Kelly, A. G.; O'Suilleabhain, D.; Gabbett, C.; Coleman, J. N. The Electrical Conductivity of Solution-Processed Nanosheet Networks. *Nature Reviews Materials*. Nature Research March 1, 2022, pp 217–234. DOI: <https://doi.org/10.1038/s41578-021-00386-w>
- [2] Mack, E. A., Cadranel, A., Harrer, E., Zhou, X., Wu, M., Lourenço, L. M. O., Zahn, D., Spiecker, E., Backes, C., & Guldi, D. M. (2025). Morphological and Electronic Control of Interfacial Charge Transfer in 2D Transition Metal Dichalcogenide Hybrids. *ACS Nano*. <https://doi.org/10.1021/acsnano.5c07850>

Insights to self-metalation of tetraphenyl transdibenzoporphyrin on Cu (111)

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The adsorption behavior and self-metalation of tetraphenyltransdibenzoporphyrin (2H-TPtdBP) on Cu(111) at various temperatures and coverages have been investigated by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and density-functional theory (DFT) calculations [1,2]. When deposited at low coverages (<0.16 molecules nm^{-2}), the free-base molecules adsorbed as isolated individual molecules with an inverted conformation, and no self-metalation was observed upon annealing up to 363 K. At higher coverages, the free-base molecules self-metalated already at room temperature, and to a larger extent at 363 K, forming ordered islands of Cu-TPtdBP. Annealing at 423 K led to the complete self-metalation up to a full monolayer coverage. The comparison of the results of this study with the published literature demonstrates, how the selection of the substituents affects the self-metalation of tetraphenyl-based porphyrins.

[1] Majid Shaker et al. 2025 J. Phys.: Condens. Matter 37 085001.

[2] Maximilian Muth et al. 2025 Chem. Eur. J., 31: e202500998.

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Decoding Shake-up Satellites in XPS: Spectral Signatures of Ring Fusion in Porphyrins

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Shake-up satellites in X-ray photoelectron spectroscopy (XPS) arise when core ionization is accompanied by charge-neutral valence excitations. By coupling a localized core excitation to the valence manifold, these satellites can encode unique chemical information not contained in the main ionization lines. However, their interpretation is challenging due to low intensity and intrinsic many-body character, and gold-standard approaches for XP spectra such as GW fail to predict satellite features accurately. Here we address this limitation by means of our recently developed *GW*+cumulant expansion approach (*GW+C*) [1]. We apply this framework to N 1s core-level spectra of a series of tetraphenylporphyrin derivatives with consecutively fused phenyl rings, achieving excellent agreement with measured satellite intensities and positions within 0.2 eV. We find that ring fusion strongly reshapes the satellite manifold, while the N 1s main line remains comparatively unchanged. The simulations resolve the origin of individual satellites and establish precise correlations between structural modifications and spectral changes. In sum, we show how *ab initio* simulations can decode complex satellite structure in XP spectra and thereby unlock information previously inaccessible from experiment alone.

References

[1] J. Kockläuner and D. Golze, *J. Chem. Theory Comput.* 2025, 21, 6, 3101–3119.

Gyromagnetic ratio reduction toward long coherence time in 2D c-MOFs based spin array

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Organic two-dimensional crystals (O2DCs) have emerged as a versatile platform for developing the next generation of electronic and quantum technologies.¹ Built from π -conjugated ligands, these VdW layered structure combine strong in plane bonding and high chemical tunability. Two-dimensional conjugated metal-organic framework (2D c-MOF) is a subset of O2DCs in which the conjugated ligand is oxidized and coordinated to metal centers.² Through the partial oxidation of the ligand during the material synthesis, a semiquinone like radical is formed, offering a promising platform for highly crystalline radical based spin qubit arrays.³ Two essential parameters representing the qubit performance are the spin-lattice relaxation time constant (T_1) and the spin-spin decoherence time constant (T_2), the latter represent the effective operation time of a qubit. Several phenomena limit those constants, hyperfine interaction, occurring through the coupling between an electronic spin and a nuclear spin leads to decoherence.⁴

In this work, the reduction of the hyperfine interaction between the free radical qubit and the nuclear spin embedded in the structure is achieved through hydrogen-deuterium substitution, leading to an extended decoherent time constant. Structural, spectroscopic, and spin-dynamics investigations confirm the successful synthesis of stable crystalline 2D c-MOFs incorporating deuterated ligands. Importantly, spin resonance measurements reveal record values for coherence times in these systems.^{3,5} This developments illustrates how rational design and bottom-up design strategy can help to achieve extend the structural and functional diversity of organic 2D crystals.

References

1. Wang, Z., Wang, M., Heine, T. & Feng, X. Electronic and quantum properties of organic two-dimensional crystals. *Nat Rev Mater* **10**, 147–166 (2024).
2. Wang, M., Dong, R. & Feng, X. Two-dimensional conjugated metal–organic frameworks (2D c-MOFs): chemistry and function for MOFtronics. *Chem. Soc. Rev.* **50**, 2764–2793 (2021).
3. Lu, Y. *et al.* Rational Construction of Layered Two-Dimensional Conjugated Metal–Organic Frameworks with Room-Temperature Quantum Coherence. *J. Am. Chem. Soc.* **147**, 8778–8784 (2025).
4. Oanta, A. K. *et al.* Electronic Spin Qubit Candidates Arrayed within Layered Two-Dimensional Polymers. *J. Am. Chem. Soc.* **145**, 689–696 (2023).
5. Zhou, A. *et al.* Phononic modulation of spin-lattice relaxation in molecular qubit frameworks. *Nat Commun* **15**, 10763 (2024).

Photoluminescence Study of Optical Transitions in Two-Dimensional TMD Semiconductors

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Transition metal dichalcogenides (TMDCs), with the general formula MX_2 are semiconductors in which M denotes a transition metal atom (such as Mo or W) and X represents a chalcogen atom (such as S, Se, or Te) [1][2]. Unlike graphene, TMDC crystals exhibit band gaps, demonstrating semiconducting behavior[3]. As the material layers decreases from bulk to a monolayer, the band gap changes from indirect to direct[4].

Photoluminescence (PL) studies of two-dimensional TMDCs provide valuable information about their electronic and optical properties[1][2]. A new Setup, which is so-called squeezable nanojunction (SNJ), enables optical characterization of two approaching monolayers[5][6] (e.g., MoS_2 - MoS_2 , WS_2 - WS_2 and MoS_2 - WS_2). These experiments open exciting opportunities for gaining new insights into interlayer coupling and heterostructure physics.

References

[1] Wang, Q., Kalantar-Zadeh, K., Kis, A. et al. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nature Nanotech* 7, 699–712 (2012).

[2] Manzeli, S., Ovchinnikov, D., Pasquier, D. et al. 2D transition metal dichalcogenides. *Nat Rev Mater* 2, 17033 (2017).

[3] Chhowalla, M., Shin, H., Eda, G. et al. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nature Chem* 5, 263–275 (2013).

[4] Splendiani et al., *Nano Lett.*, 2010.

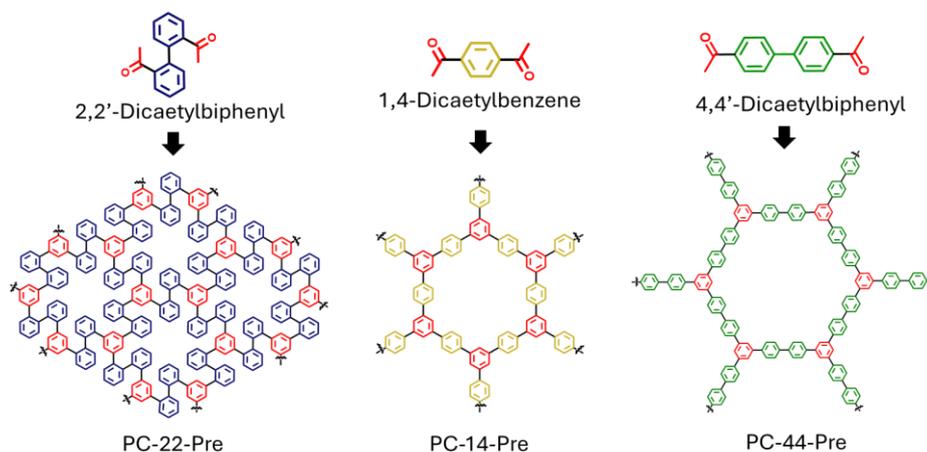
[5] M. A. Popp and H. B. Weber. An ultra-stable setup for measuring electrical and thermoelectrical properties of nanojunctions. *Applied Physics Letters*, 115(8):083108, 2019.

[6] M.A. Popp, A. Erpenbeck, and H.B. Weber. Thermoelectricity of nearresonant tunnel junctions and their relation to carnot efficiency. *Sci Rep*, 11:2031, 2021.

Structural and Thermal Control of Porous Carbon Properties from Aldol Condensation-derived Polymer Precursors

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Porous carbon materials are considered ideal electrode material candidates for electric double-layer capacitors (EDLCs) owing to their high surface area, electrical conductivity, and chemical stability. Among the various synthetic approaches for porous carbons, the use of conjugated synthetic polymers as precursors offers distinct advantages, as it allows molecular-level control over doping, porosity, etc. and enables precise tuning of the resulting carbon properties for enhanced electrochemical performance.¹ A systematic study is presented on the properties of carbon materials synthesized from conjugated polymers obtained via the triple aldol condensation reaction on three diacetyl-containing compounds: 2,2'-diacetylbiphenyl, 4,4'-diacetylbiphenyl, and 1,4-diacetylbenzene. The aldol condensation reaction of these acetyl-functionalized molecules yields highly conjugated polymeric frameworks that serve as efficient precursors for carbon materials, producing good yields upon high-temperature pyrolysis.^{2,3} The three precursors differ in their molecular frameworks and extent of conjugation, allowing an investigation of the relationship between precursor structure, graphitization, and porosity in the resulting carbons. Our results demonstrate that the degree of graphitization is influenced primarily by pyrolysis temperature rather than precursor structure. However, structural effects become increasingly significant at lower carbonization temperatures, where conjugation and framework rigidity appear to play a role in graphitic ordering. In contrast, the porosity of the carbon materials is more directly correlated with the structural characteristics of the precursor polymers, reflecting the differences in their molecular architecture. These findings highlight the importance of precursor design in tailoring porosity, while temperature remains the dominant factor in controlling graphitization.



References

[1] Xu, F.; Wu, D.; Fu, R.; Wei, B. Design and Preparation of Porous Carbons from Conjugated Polymer Precursors. *Materials Today* **2017**, *20* (10), 629–656.

[2] Che, S.; Li, C.; Wang, C.; Zaheer, W.; Ji, X.; Phillips, B.; Gurbandurdyev, G.; Glynn, J.; Guo, Z.-H.; Al-Hashimi, M.; Zhou, H.-C.; Banerjee, S.; Fang, L. Solution-Processable Porous Graphitic Carbon from Bottom-up Synthesis and Low-Temperature Graphitization. *Chem. Sci.* **2021**, *12* (24), 8438–8444.

[3] Rose, M.; Klein, N.; Senkovska, I.; Schrage, C.; Wollmann, P.; Böhlmann, W.; Böhringer, B.; Fichtner, S.; Kaskel, S. A New Route to Porous Monolithic Organic Frameworks via Cyclotrimerization. *J. Mater. Chem.* **2010**, *21* (3), 711–716.

Chitin/Graphene Oxide Composite Materials for Heavy Metal Ion Adsorption

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Rare earth elements (REEs) are vital to modern technology due to their unique properties and widespread industrial applications. However, their growing utilization results in increased environmental release, raising concerns regarding potential ecological impacts and human health risks. Efficient removal of REEs from wastewater, particularly in mining and nuclear industry, is thus crucial. Recycling these elements has emerged as a sustainable approach for wastewater processing and waste reuse. The present study focuses on developing composite adsorbents for this application, as adsorption presents advantageous properties for effective contaminant removal. Chitin, a biopolymer derived from marine waste, is a particularly promising adsorbent. Its availability, low cost, biocompatibility, and biodegradability qualify it as potent material. However, the processing of chitin into stable materials is challenging due to its very low solubility. Previously, we reported the cross-linking of α -chitin with its monomer by processing in the ionic liquid (IL) 1-butyl-3-methylimidazolium acetate. These composites, however, show a decreased adsorption capacity due to partial blocking of adsorption sites. To overcome this problem, we have now incorporated graphene oxide (GO) into the chitin-based composite. With its large surface area and various functional groups, GO even improves the favorable properties of chitin. These composites are shown to very efficiently remove even spurious REE amounts from aqueous solutions.

References

- [1] Tanner, H. Chanzy, M. Vincendon, J. C. Roux and F. Gaill, *Macromolecules*, **23**, 3576 (1990).
- [2] G. Cárdenas, G. Cabrera, E. Taboada and S. P. Miranda, *J. Appl. Polym. Sci.*, **93**, 1876 (2004).
- [3] E. Brunner, H. Ehrlich, P. Schupp, R. Hedrich, S. Hunoldt, M. Kammer, S. Machill, S. Paasch, V. V. Bazhenov, D. V. Kurek, T. Arnold, S. Brockmann, M. Ruhnnow and R. Born, *J. Struct. Biol.*, **168**, 539 (2009).
- [4] F. G. Pearson, R. H. Marchessault and C. Y. Liang, *J. Polym. Sci.*, **43**, 101–116 (1960).
- [5] B. Focher, A. Naggi, G. Torri, A. Cosani and M. Terbojevich, *Carbohydr. Polym.*, **18**, 43 (1992).
- [6] H.-L. Guo, X.-F. Wang, Q.-Y. Qian, F.-B. Wang and X.-H. Xia, *ACS Nano*, **3**, 2653 (2009).
- [7] Z. Mo, Y. Sun, H. Chen, P. Zhang, D. Zuo, Y. Liu and H. Li, *Polymer*, 2005, **46**, 12670.
- [8] L. Shahriary, H. Ghourchian and A. A. Athawale, *J. Nanotechnol.*, **2014**, 2014, 1.
- [9] A. Aravind, K. Seliverstova, K. K. K. Kammerlander, T. Henle and E. Brunner, *Int. J. Mol. Sci.*, **26**, 3149 (2025).

Highly Efficient Functionalization and Covalent Patterning of Graphene by Photoactivation

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Since its first isolation, graphene has remained at the forefront of materials research owing to its remarkable electronic, mechanical, and optical properties.^[1-2] These unique characteristics hold the potential to revolutionize material applications similar to how polymers did in the past. However, its practical implementation is hindered by poor processability, arising from insolubility, and by the absence of an intrinsic bandgap, which limits its use in electronic devices such as transistors. To overcome these limitations, structural modification strategies have been explored, with chemical functionalization emerging as particularly promising. Covalent grafting of functional groups onto graphene can enhance its dispersibility and induce a tunable bandgap, thereby tailoring its properties for specific applications.^[3-4] Yet, the high chemical inertness of graphene renders covalent modification challenging. Although various reactions on the carbon lattice have been reported, functionalization yields are typically low, and efficient modification often requires harsh conditions, such as plasma treatment, electrochemical activation, or the use of strong reducing agents, which demand specialized equipment and expertise.^[5-7] Consequently, accessible and efficient routes for the covalent modification of substrate-supported graphene remain scarce. Herein, we present a facile and scalable approach for the light-induced covalent functionalization of graphene employing non-toxic and readily available iodonium salts as active reagents. Upon photoexcitation of graphene, the planar carbon lattice reacts efficiently with these reagents, affording high functionalization yields under mild reaction conditions. Furthermore, spatially controlled modification with micrometer-scale resolution is achieved, enabling the integration of pristine and functionalized regions within a single sample. This method offers a versatile and accessible platform for tailoring graphene's properties towards future applications.

References

- [1] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, 6, 183-191.
- [2] K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, *Nature* **2012**, 490, 192-200.
- [3] C. K. Chua, M. Pumera, *Chem. Soc. Rev.* 2013, 42, 3222-3233.
- [4] M. F. Craciun, I. Khrapach, M. D. Barnes, S. Russo, *J. Phys.: Condens. Matter* **2013**, 25, 423201.
- [5] D. C. Elias, R. R. Nair, T. M. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim, K. S. Novoselov, *Science* **2009**, 323, 610-613.
- [6] C. K. Chan, T. E. Beechem, T. Ohta, M. T. Brumbach, D. R. Wheeler, K. J. Stevenson, *J. Phys. Chem. C* **2013**, 117, 12038-12044.
- [7] J. M. Englert, C. Dotzer, G. Yang, M. Schmid, C. Papp, J. M. Gottfried, H. P. Steinrück, E. Spiecker, F. Hauke, A. Hirsch, *Nat. Chem.* **2011**, 3, 279-286.

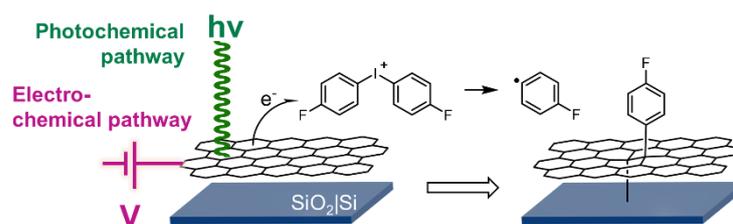
Photoelectrochemical Functionalisation of Graphene

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The modification of graphene by introducing covalently bonded functional groups to the basal plane is a key strategy for tuning its electronic and chemical properties. Both laser-induced and electrochemical techniques have been reported using iodonium salt precursors.^[1,2] By combining these two functionalisation pathways into a photoelectrochemical route, we integrate the advantages of both strategies and expand the toolbox for achieving high-precision functionalisation.

Lateral control over the modified area is obtained through the 'laser-writing' procedure, while the degree of functionalisation can be tuned by the applied electric potential. The analysis of the D- to G-band intensity ratio in the Raman spectrum reveals varying degrees of functionalisation, ranging from very high ($I_D/I_G = 2.5$) to complete suppression of surface modification ($I_D/I_G = 0$). Consequently, the ability to modulate the influence of the laser through the applied electric potential enables the use of Raman spectroscopy as a non-invasive, *in-situ* characterisation method for covalently functionalised graphene.

References

- [1] K. Gerein, D. Unmu Dzujah, H. Yu, F. Hauke, T. Heine, A. Hirsch, T. Wei, *Angew. Chem. Int. Ed.* **2024**, 63, e202414090.
 [2] T. Nagel, S. Wolff, S. Feng, H. Weber, J. Maultzsch, F. Hauke, A. Hirsch, *Carbon* **2025**, 241, 120376.

Towards precision controlled 2D functional group patterning of graphene via laser writing

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The chemical structuring of 2D materials such as graphene enables the specific tailoring of its outstanding properties and due to this, is of uttermost interest for the development of high-performance 2D materials. By applying covalent functionalization with local control, adjacent domains with altering chemical and physical properties can be generated, allowing for a complex pattern design. The so-called laser 'writing' is one of the most promising approaches to achieve this goal. Here, a chemical reaction is locally triggered by a freely movable stimulus such as laser irradiation, allowing for a site-selective functionalization of graphene. We herein present a significant advance in the understanding of the reaction mechanism and the influence of the laser 'writing' parameters in the laser-triggered activation of dibenzoyl peroxide (DBPO) and the subsequent high-precision covalent patterning of functional groups on monolayer graphene.^[1-2]

References

[1] T. Nagel et al. *Carbon*, **2025**, 241, 120376.[2] T. Nagel et al. *Adv. Sci.* **2025**, e11481

Spatially Resolved 2D Laser Writing on Graphene and SWCNT's

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The direct laser writing technique stands out as a straightforward and facile method to graft different functional moieties onto the graphene surface and therefore tuning its chemical properties.^[1-2] For the first time, we present a laser writing protocol for the spatially resolved functionalization of graphene with three structurally different diazonium salts, bearing distinct electronic characteristics. The novelty of this facile approach lies in the properties of our solid/solid phase system, which deviates significantly from conventional functionalization methods for diazonium salts that typically rely on solution-based processes.^[3] Furthermore, we successfully transferred the well-established laser writing protocol to covalently functionalize a thin film of single-walled carbon nanotubes (SWCNT's) with lateral precision using different organic precursors.

References

[1] T. Wei, F. Hauke, A. Hirsch, *Adv. Mater.* **2021**, 33, 2104060.[2] K. F. Edelthammer, D. Dasler, L. Jurkiewicz, T. Nagel, S. Al-Fogra, F. Hauke, A. Hirsch, *Angew. Chem. Int. Ed.* **2020**, 59, 23329-23334.[3] J. Krüger, T. Nagel, B. Yang, F. Hauke, A. Hirsch, *Chem. Eur. J.* **2025**, 0, e02468.

Visible Light-Responsive Photo-switching HTI (Hemithioindigo) SAMs on Surface

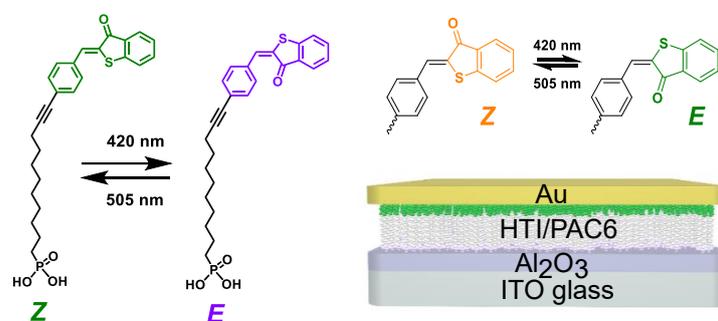
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HTI (Hemithioindigo) chromophores exhibit reversible photoisomerization between E- and Z-isomers under visible light, with high quantum yields[1]. By attaching phosphonic acid groups to HTI, self-assembled monolayers (SAMs) can be formed on aluminum oxide surfaces, ensuring stable adsorption[2,3]. Light-induced changes in the configuration of these HTI SAMs alter their dipole moments, thereby affecting surface potentials. By forming the of binary SAM systems with secondary supporting SAM molecules with different functionalities was considered to **optimize reversible photo-switching performance on surface** by providing additional degrees of freedom. This effect is anticipated to enable control of capacitance corresponding to the changes in dipole moments. Such control leads to novel functionalities[4,5], including the reversible modulation and precise control of a device's electric signaling properties using visible light.



References

[1] S. Wiedbrauk, and H. Dube. et al, *Tetrahedron Letters* 56.29 (2015): 4266-4274

[2] a) T. Bauer, et al., *ACS Appl. Mater. Interfaces* 5.13 (2013): 6073–6080 b) H. Dietrich, et al., *Physical Chemistry Chemical Physics* 19.7 (2017): 5137-44

[3] a) Q. Shen, Qian, et al., *Advanced Materials* 22.30 (2010): 3282-3287 b) Y. Wang, Ye, et al., *ACS nano* 15.8 (2021): 13732-13741

[4] a) A. Khassanov, et al., *Accounts of chemical research* 48.7 (2015): 1901-1908 b) T. Schmaltz, et al., *ACS nano* 11.9 (2017): 8747-8757

[5] A. Khassanov, et al., *Accounts of chemical research* 48.7 (2015): 1901-1908

Structural and electronic properties of NBD-derivative on Au(111) & Graphene/Ir(111)

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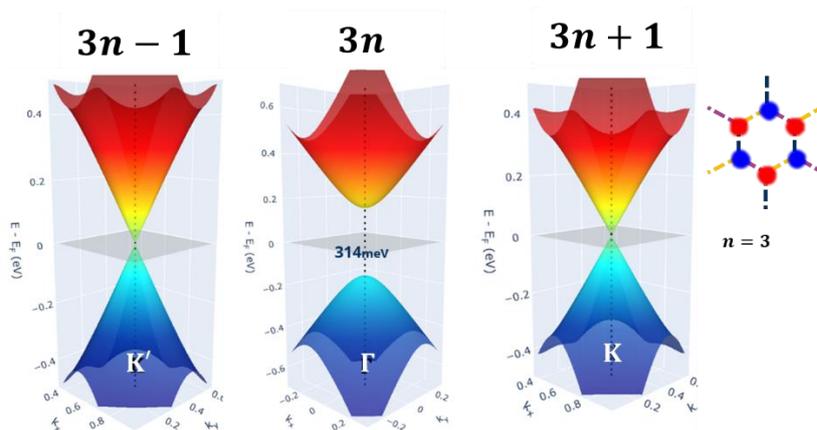
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An intriguing class of molecular photoswitches is norbornadiene/quadracyclane (NBD/QC), where low-energy NBD can be converted to its metastable isomer QC using external energy, typically in the form of light. The NBD/QC system has been reported quite extensively in solution-based environment, while the on-surface studies remain limited [1]. Unlike in the gas/liquid phase, NBD can have different adsorption conformations on a surface, resulting in different interactions with the surface. In this work, we discuss the self-assembly and electronic properties of a benzoic acid-functionalized NBD on Au(111) using scanning tunneling microscopy/spectroscopy (STM/STS) complemented by density functional theory (DFT) calculations. We observed two distinct adsorption conformations, although the molecular arrangement based on dimeric hydrogen bonding between the terminal carboxyl groups remains the same. To gain insight into molecule-substrate interactions, we also studied the molecular self-assembly on graphene/Ir(111), with graphene acting as a decoupling layer [2]. In contrast to Au(111), we observed an additional hydrogen-bonding motif between the NBD derivatives. Additionally, differences in the electronic properties were detected. Our study highlights the critical role of substrate selection for studying the properties of the NBD derivatives and provides insight into optimizing their switching performance when interfaced with another (inorganic) material.

References

- [1] Hemauer, F.; Steinrück, H.-P.; Papp, C., The Norbornadiene/Quadracyclane Pair as Molecular Solar Thermal Energy Storage System: Surface Science Investigations. *ChemPhysChem* 2024, 25, e202300806, DOI: <https://doi.org/10.1002/cphc.202300806>.
- [2] Maier, S.; Stöhr, M., Molecular assemblies on surfaces: towards physical and electronic decoupling of organic molecules. *Beilstein Journal of Nanotechnology* 2021, 12, 950-956, DOI: 10.3762/bjnano.12.71.

Controlling the electronic properties of graphene superlattices with periodic vacancy

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Graphene is one of the 2D materials with excellent properties due to the presence of the Dirac cone^[1]. However, the lack of a band gap and intrinsic spin polarization limits its applications^[2]. The periodic vacancies with various symmetries were introduced periodically in the graphene superlattice in the Tight-Binding level^[3], considering only the first nearest neighbor. The intervalley coupling is needed in order to open the gap in graphene. The graphene with $A = B$ vacancy can open the gap if the superlattice size is $3n \times 3n$ where n is the number of the repeating unit cell, and the vacancy containing C_3 symmetry, such as C_3 , D_{3h} , D_{6h} , causing the K and K' valleys to be folded into Γ as shown in Fig. 1, which is required for the intervalley coupling to occur. Other types of vacancy, like C_1 and C_2 cannot open the gap, but only cause the shift of the Dirac cone to the lower symmetry point. The band gap of a graphene with patterned vacancy is increasing with the defect concentration. On the other hand, the $A \neq B$ vacancy in graphene superlattices can induce a flat band, which is a sign of the presence of magnetic properties. The electronic and magnetic properties of graphene superlattice can be controlled by the rational guidelines that we established.

References

- [1] K. S. Novoselov, et al., *Science*, 2004, 306, 666.
 [2] A. H. Castro Neto, et. al., *Rev. Mod. Phys.*, 2009, 81, 109–162.
 [3] S. Reich, et. al., *Phys. Rev. B*, 2002, 66, 035412.