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# Overcoming Synthetic Challenges in Pyrazinacene-conjugated Polymers: A Breakthrough in n-Type Polymer Materials

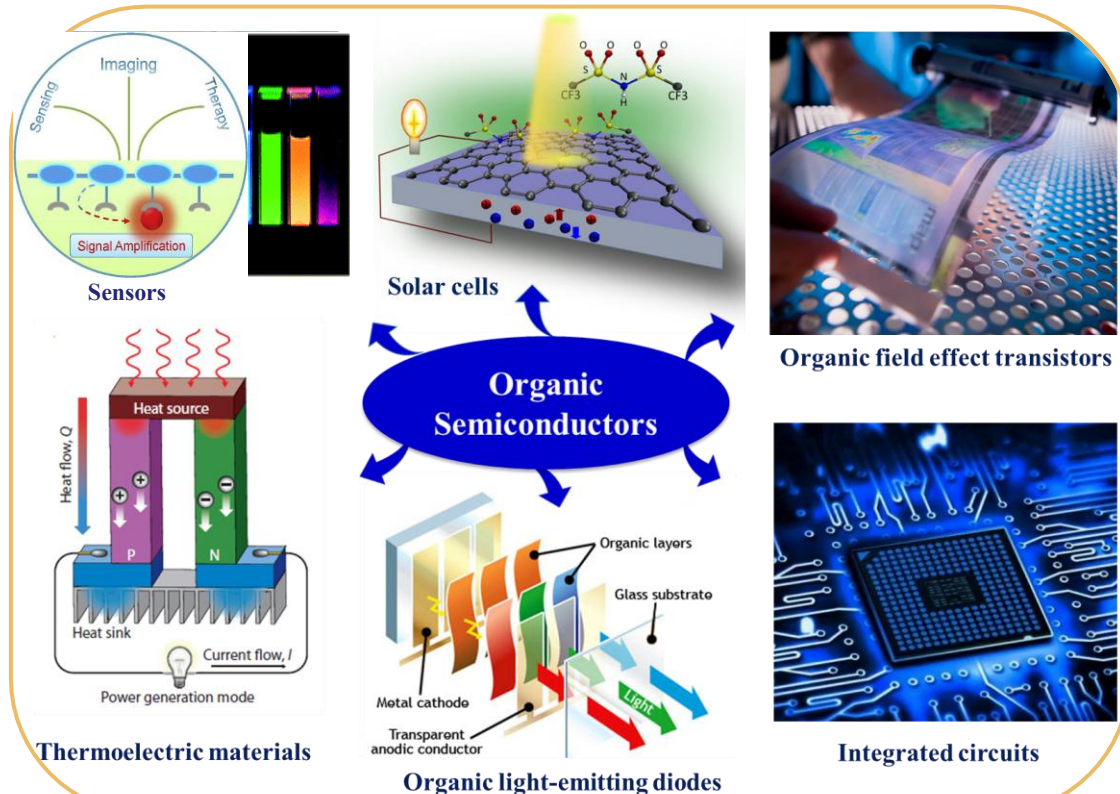
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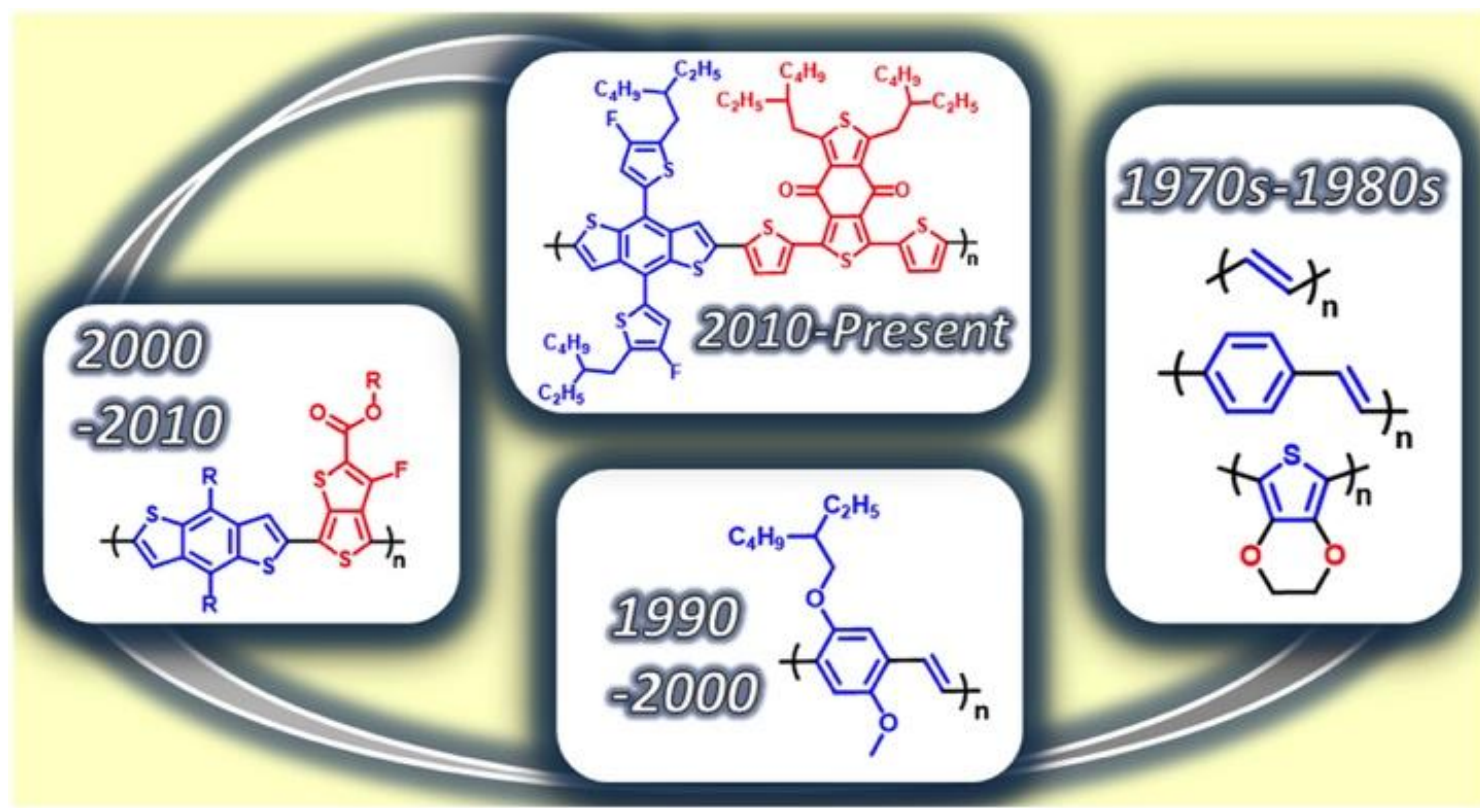


## Organic Semiconductors



Nano-Micro Lett. **2023**, 15, 105. Organic Thermoelectric Devices Springer, **2022** pp 235–259. J. Appl. Phys. **1989**, 65, 3610. Nano Lett. **2012**, 12, 2745–2750. Nanotechnology. **2012**, 23, 385308. Academic Journal of Science and Technology. **2023**, 7(3), 148–150. Chem. **2017**, 2, 760–790

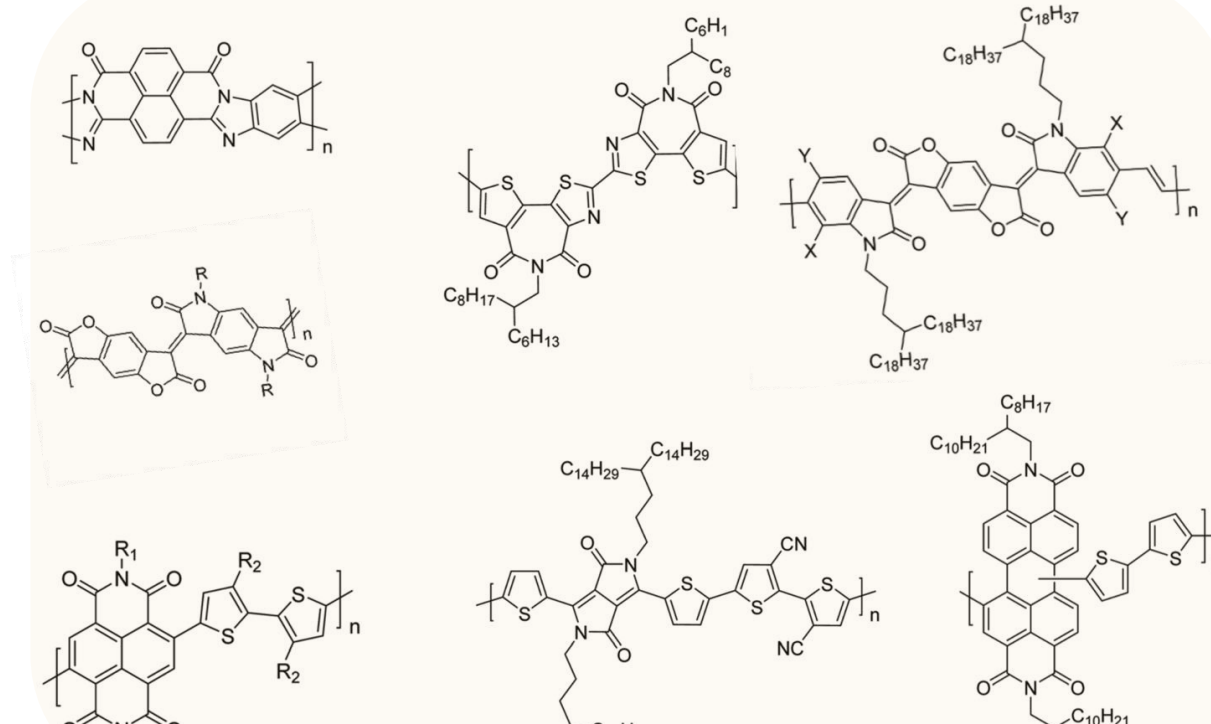
## The p-Type Dominance in $\pi$ -Conjugated Polymers



Polymer, **2020**, 207, 122874

## Shifting the Paradigm:

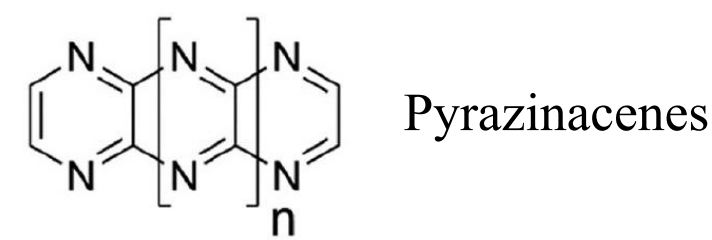
### Toward n-Type $\pi$ -Conjugated Polymers



J. Mater. Chem. A, **2021**, 9, 5149; J. Mater. Chem. C, **2021**, 9, 8099

## n-Type Acenes:

### An Untapped Reservoir for Polymer Innovation



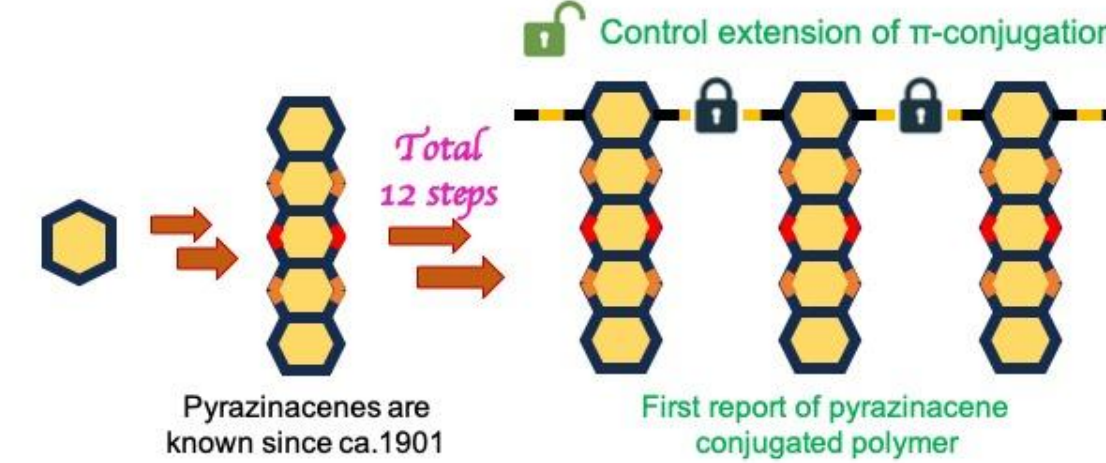
Pyrazinacenes

- Nitrogen-rich backbone.
- Electron-deficient backbone enhance their performance in organic optoelectronic devices.
- Demonstrated ability to sense cations, anions, and biomolecules.
- Useful n-type materials with low-lying LUMOs.

**No report of pyrazinacene polymers**

Acc. Chem. Res., **2021**, 54, 3228; Org. Lett., **2012**, 14, 4190; Angew. Chem. Int. Ed., **2013**, 52, 3810

## This Work

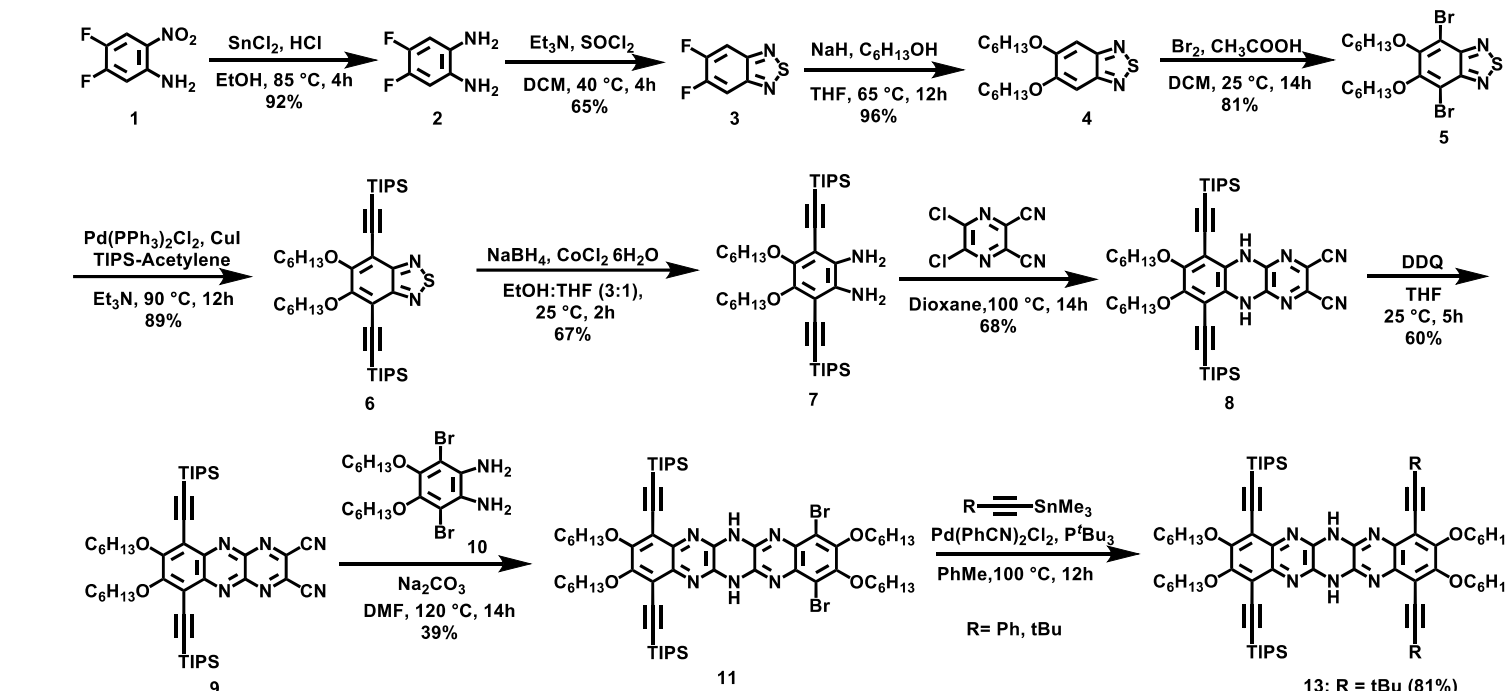


- First report of pyrazinacene conjugated polymers since the discovery of pyrazinacene in 1901.
- Nitrogen-rich (electron-deficient) backbone.

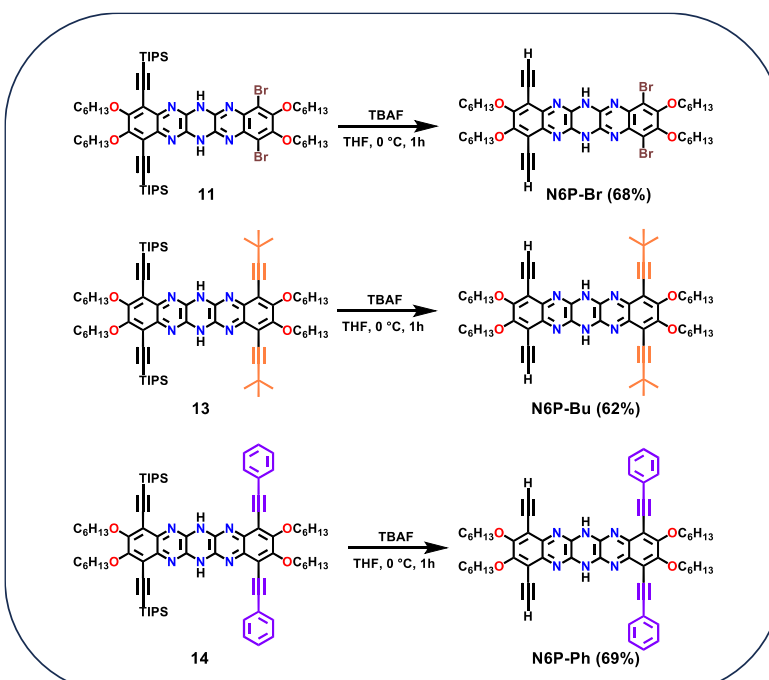
Chem. Sci. **2024**, 15, 4054–4067, DOI: 10.1039/D3SC06552A

## Pyrazinacene Monomer Synthesis

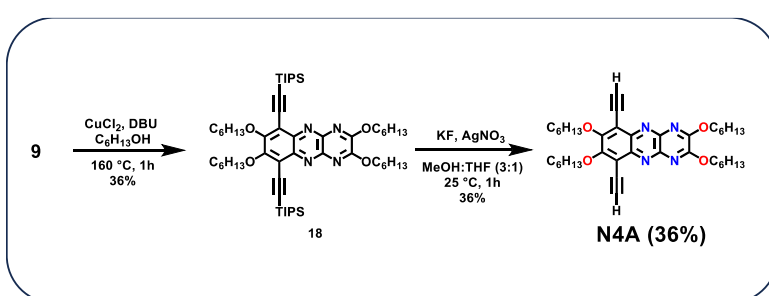
### Monomer Synthesis



### 5 Fused Ring systems

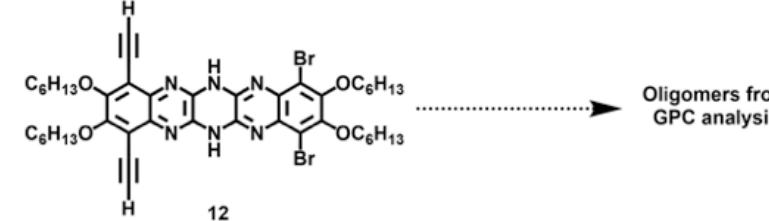


### 3 Fused Ring System



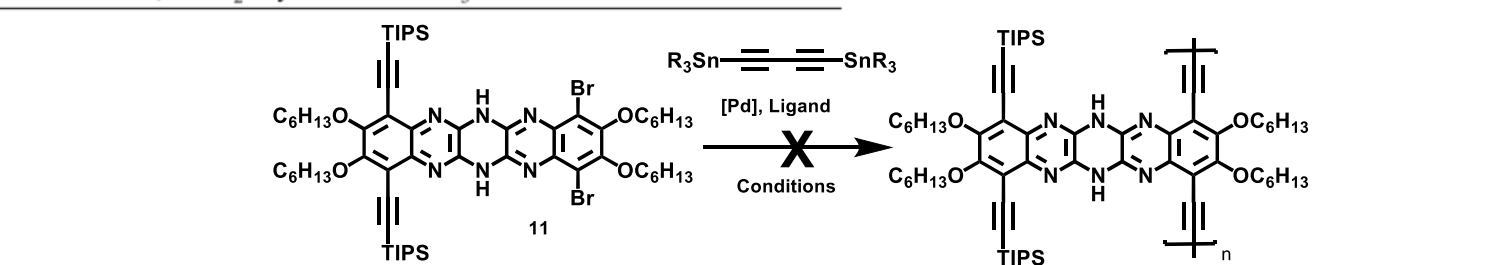
- Successfully synthesized pyrazinacene monomers containing solubilizing alkyl chains for solution-processability.
- Introduced pendant groups (Br, Bu, Ph) to probe their electronic and optical influence.

### Polymerization Attempts



Entry	[Cu]	Base	Solvent	Temp	Time (h)	Result
1	CuCl	TMEDA	CH <sub>2</sub> Cl <sub>2</sub>	35 °C	48	SM isolated
2	CuCl	TMEDA	PhMe: ACN (2:1)	55 °C	24	SM isolated
3	Cu(OAc) <sub>2</sub>	Pyridine	PhMe	25 °C	24	SM isolated
4	CuCl, CuCl <sub>2</sub>	Pyridine	CH <sub>2</sub> Cl <sub>2</sub>	25 °C	7	SM isolated
5	CuCl, CuCl <sub>2</sub>	Pyridine	CHCl <sub>3</sub>	50 °C	4	SM isolated

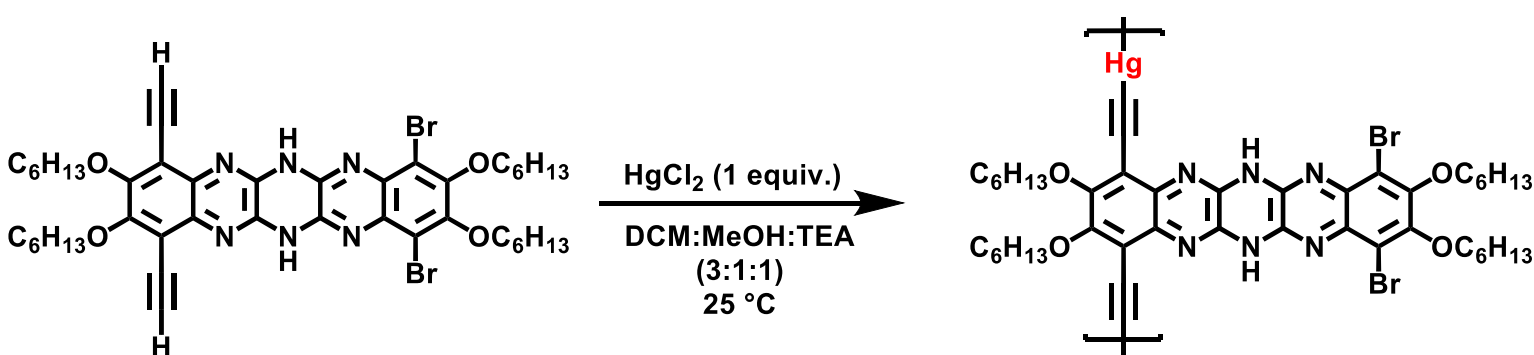
Conventional Pd- and Cu-catalyzed polymerizations consistently failed or yielded only insoluble oligomers—highlighting the incompatibility of standard cross-coupling protocols with pyrazinacene substrates.



Entry	[Pd]	Ligand	Additive	Solvent	Temp	Time (h)	Result
1	Pd(dba) <sub>3</sub>	PPH <sub>3</sub>	---	PhMe	100 °C	96	SM isolated
2	Pd(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Cl <sub>2</sub>	P(Cu) <sub>3</sub>	---	PhMe	100 °C	120	SM isolated
3	Pd(PPh <sub>3</sub> ) <sub>4</sub>	---	---	PhMe	110 °C	96	SM isolated
4	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	PPH <sub>3</sub>	CuI	DMF	80 °C	19	Insol. ppt. found
5	Pd(PPh <sub>3</sub> ) <sub>4</sub>	---	---	DMF	80 °C	24	SM isolated
6	Pd(Bu <sub>3</sub> P) <sub>2</sub>	---	K <sub>3</sub> PO <sub>4</sub>	PhMe	100 °C	48	SM isolated

## A Breakthrough in Pyrazinacene Polymerization

### Metal Mediated Unconventional Step-Growth Polymerization Mechanism



### Optimizing the Polymerization Conditions

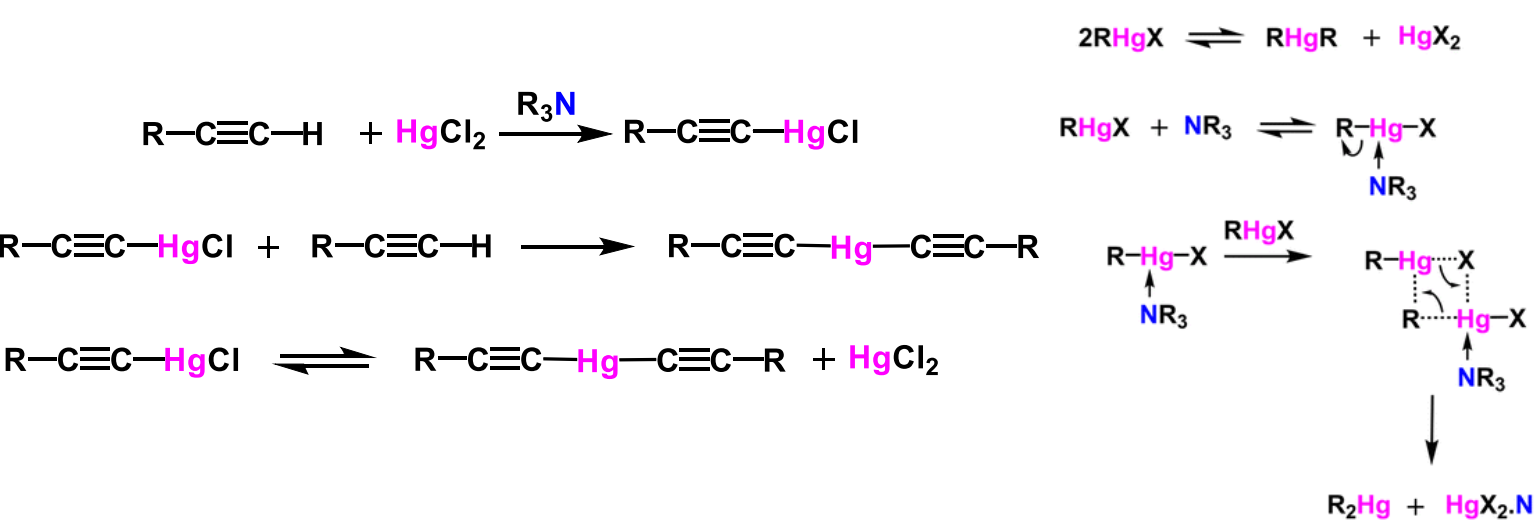
Entry	Base	Time (h)	M <sub>n</sub> /M <sub>w</sub> (kDa)	X <sub>n</sub> /X <sub>w</sub>	D
1	Diisopropylamine	1	12/18	11/16	1.5
2	Tetramethylethylenediamine	1	11/14	10/13	1.2
3	Diisopropylethylamine	1	12/18	11/16	1.5
4	Pyridine	1	9/11	8/10	1.2
5	Piperidine	1	11/16	10/15	1.4
6	Triethylamine	1	14/21	13/19	1.5

### HgCl<sub>2</sub> Equivalents Optimization

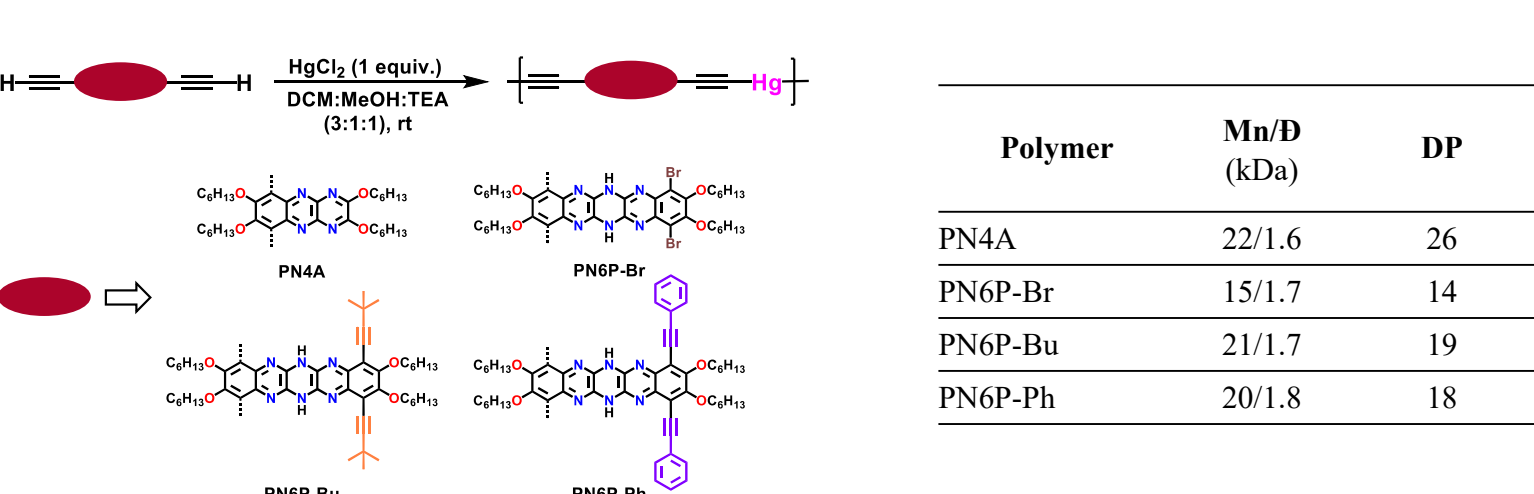
Entry	HgCl <sub>2</sub> (equiv)	Time (h)	M <sub>n</sub> /M <sub>w</sub> (kDa)	X <sub>n</sub> /X <sub>w</sub>	D
1	0.50	1	8/13	7/12	1.2
2	0.75	1	14/25	13/23	1.8
3	1.0	1	14/21	13/19	1.5
4	1.25	1	20/45	18/41	2.3
5	1.50	1	19/31	17/28	1.6

Where M<sub>n</sub> is the number average molecular weight, M<sub>w</sub> is the weight average molecular weight, X<sub>n</sub> is number average degree of polymerization, X<sub>w</sub> is weight average degree of polymerization and D is the polydispersity index. All reactions were performed with 10 mg of SM (1 eq.) at RT. All GPCs were reported after washing with MeOH (Dacryl) filter. Polymer molecular weight were determined using gel permeation chromatography (tetrahydrofuran as the eluent) against polystyrene standards.

### Polymerization Mechanism

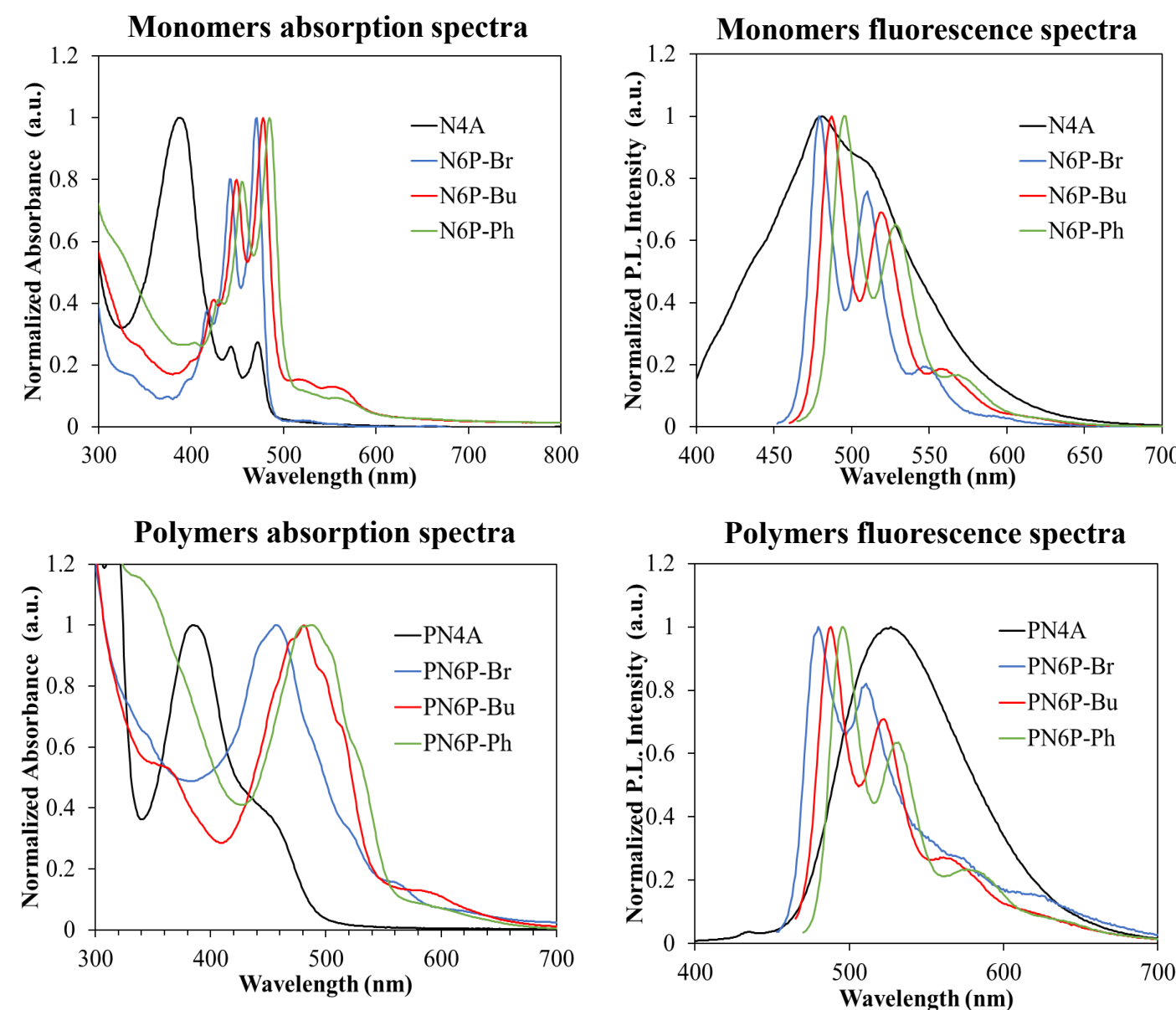


### Synthesis of Series of Pyrazinacene Polymers



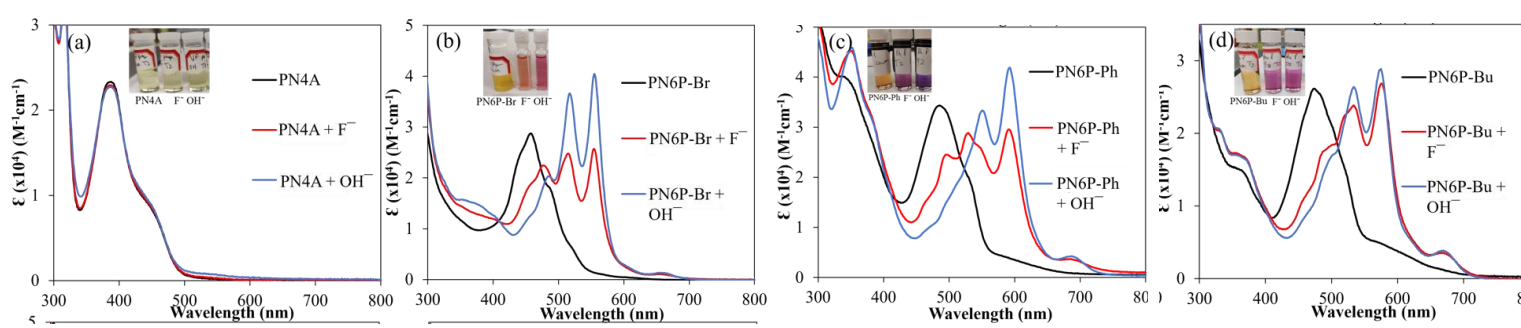
- Overcame limitations of Pd- and Cu-based coupling reactions using Hg(II).
- Polymerization proceeds at RT and accommodates non-stoichiometric monomer ratios.
- Hg(II) plays a dual role: forming acetylide complexes and promoting RHgCl self-condensation, enabling efficient chain growth.

## Optical Properties of Monomers and Polymers



- Polymerization red-shifts absorption by ~100 nm relative to monomers, confirming backbone conjugation extension.

### Anion Dependent UV-Vis Absorption Spectra of Pyrazinacene Polymers



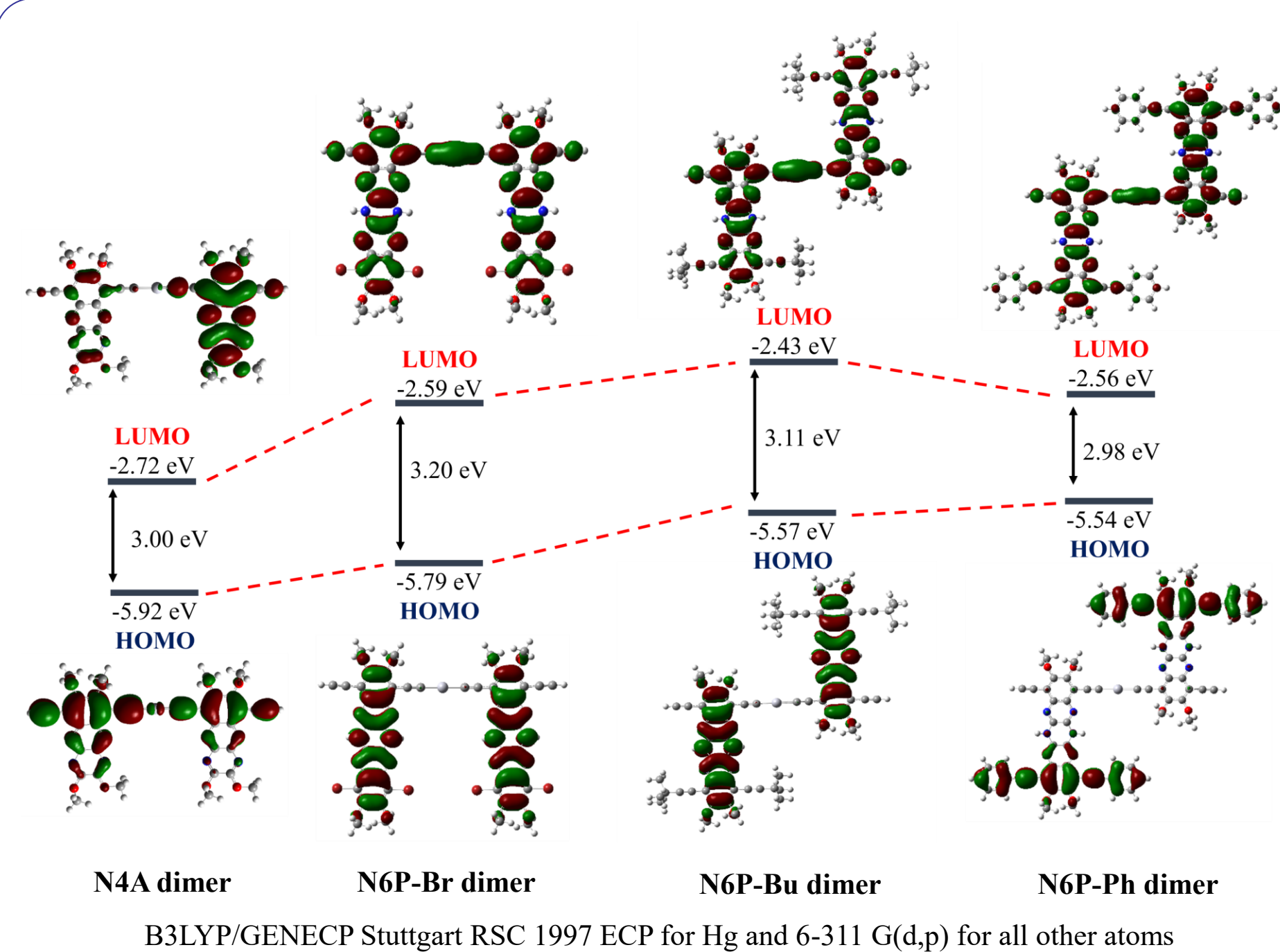
- Ion-responsive NH protons on dihydropyrazine rings enable anion-induced chromic shifts.
- No significant response in oxidized PN4A, confirming specificity of NH protons in pyrazinacene core.

### Comprehensive redox properties of polymers and monomers

Polymer/ TIPS Monomer	E <sub>ox</sub> <sup>onset</sup> (eV)	LUMO <sup>CV</sup> (eV)	HOMO <sup>CV</sup> (eV)
PN4A	2.31	-3.27	-5.40
18 (N4A-TIPS)	2.85	-3.02	-5.87
PN6P-Br	2.17	-4.68	-6.85
11 (N6P-Br-TIPS)	2.54	-2.70	-5.24
PN6P-Bu	2.13	-4.50	-6.63
13 (N6P-Bu-TIPS)	2.50	-2.62	-5.12
PN6P-Ph	2.21	-4.42	-6.63
14 (N6P-Ph-TIPS)	2.45	-2.70	-5.15

- Polymer LUMOs ~2 eV lower than monomers—achieved via conjugation through Hg(II) bridges.
- Two distinct reduction waves observed for all PN6P polymers (Br, Bu, Ph) indicate multi-electron accepting behavior, a hallmark of effective n-type materials.
- PN4A shows only a ~0.2 eV shift, suggesting that interunit conjugation is minimal in oxidized pyrazinacenes, reaffirming the importance of reduced dihydropyrazine units for achieving electronic delocalization across the chain.

## DFT Simulations of Pyrazinacene-dimers



- DFT and CV confirm that LUMO delocalizes through Hg(II), enabling multi-electron reductions and n-type behavior.

## Conclusion and Summary

- First report of pyrazinacene conjugated polymers since the discovery of pyrazinacene in 1901.
- Overcame limitations of Pd- and Cu-based coupling reactions using Hg(II).
- High DP realized at RT with non-equivalent monomer ratios.
- Redox state of pyrazine controls extension of conjugation between repeat units.
- Polymerization lowers LUMO by 2 eV compared to monomer.
- Polymers exhibit ionic- and halochromism.
- Capable of ion sensing, multi-electron redox, with potential in organic electronics and sensing.

## Acknowledgements



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