# Supplementary Material

# for

# *Experimental and DFT insights into the adsorption mechanism of methylene blue by alkali-modified corn straw biochar*

Huali Yu § [a], Yulu Zhang § [a], Lianfeng Wang [a, *], Ya Tuo [b], Song Yan [a], Junling Ma [a], Xue Zhang [a], Yu Shen [a], Haiyan Guo [a], Lei Han [a]

[a] School of Environmental & Chemical Engineering, Dalian Jiaotong University, Dalian 116021, China

[b] Environmental Development Center of the Ministry of Ecology and Environment, Beijing 100006, China

* Corresponding author, Lianfeng Wang

Phone/Fax: +86-411-84107585,

Email: wanglfdl@aliyun.com

§ Huali Yu and Yulu Zhang contributed equally to this paper.

*This file contains 7 tables and 8 figures.*

**Table S1.** Orthogonal experiment results and range analyses of NaOH-modified biochar.

| Sample | Pyrolysis temperature (℃) A | Solid-liquid ratio (v/w) B | NaOH concentration (M) C | Modification time (h) D | Removal efficiency (%) |
|---|---|---|---|---|---|
| C1 | 300 | 1:10 | 0.5 | 6 | 98.12 |
| C2 | 300 | 1:20 | 1 | 12 | 98.28 |
| C3 | 300 | 1:30 | 1.5 | 18 | 98.20 |
| C4 | 300 | 1:40 | 2 | 24 | 98.79 |
| C5 | 400 | 1:10 | 1 | 18 | 59.00 |
| C6 | 400 | 1:20 | 0.5 | 24 | 45.53 |
| C7 | 400 | 1:30 | 2 | 6 | 40.51 |
| C8 | 400 | 1:40 | 1.5 | 12 | 70.34 |
| C9 | 500 | 1:10 | 1.5 | 24 | 43.30 |
| C10 | 500 | 1:20 | 2 | 18 | 44.79 |
| C11 | 500 | 1:30 | 0.5 | 12 | 25.46 |
| C12 | 500 | 1:40 | 1 | 6 | 30.48 |
| C13 | 600 | 1:10 | 2 | 12 | 96.32 |
| C14 | 600 | 1:20 | 1.5 | 6 | 92.92 |
| C15 | 600 | 1:30 | 1 | 24 | 93.84 |
| C16 | 600 | 1:40 | 0.5 | 18 | 91.61 |
| $K_{1\text{-}1}$ | 98.3 | 74.2 | 65.2 | 65.5 | |
| $K_{1\text{-}2}$ | 53.8 | 70.4 | 70.4 | 72.6 | |
| $K_{1\text{-}3}$ | 36.0 | 64.5 | 76.2 | 73.4 | |
| $K_{1\text{-}4}$ | 93.7 | 72.8 | 70.1 | 70.4 | |
| Range | 62.3 | 9.7 | 11.0 | 7.9 | |
| Factor priority | A > C > B > D | | | | |
| Optimal conditions | $A_1B_1C_3D_3$: 300 ℃, 1:10, 1.5 M, and 18 h | | | | |

$K_{1\text{-}1}$~$K_{1\text{-}4}$ corresponded to the average value of different levels of factors.

**Table S2.** Results of variance analysis of NaOH-modified biochar orthogonal experiment.

| Factors | Sum of squares | Degrees of freedom | Mean square | F-value | Significance |
|---|---|---|---|---|---|
| Pyrolysis temperature (℃) | 1.112 | 3 | 0.371 | 51.496 | *** |
| Solid-liquid ratio (v/w) | 0.022 | 3 | 0.007 | 1.016 | |
| NaOH concentration (M) | 0.024 | 3 | 0.008 | 1.126 | |
| Modification time (h) | 0.015 | 3 | 0.005 | 0.7 | |

$P < 0.05$ indicated a significant difference represented by ***.

**Table S3.** Selected characteristics of $NaCBC_{300}$, $CBC_{300}$, $CBC_{400}$, $CBC_{500}$, and $CBC_{600}$.

| Species | SSA ($m^2/g$) | TPV ($cm^3/g$) | AP (nm) |
|---|---|---|---|
| $NaCBC_{300}$ | 92.005 | 0.142 | 10.239 |
| $CBC_{300}$ | 101.213 | 0.157 | 8.589 |
| $CBC_{400}$ | 148.852 | 0.169 | 7.988 |
| $CBC_{500}$ | 169.562 | 0.171 | 6.525 |
| $CBC_{600}$ | 187.137 | 0.189 | 5.834 |

**Table S4.** The location and assignments of FTIR peaks.

| No. | Location ($cm^{-1}$) | Assignments | Reference |
|---|---|---|---|
| 1 | 3408 | -OH stretch vibration | (Mayakaduwa et al., 2017) |
| 2 | 2924-2933 | C-H vibration of $-CH_x$ group | (Rong et al., 2020) |
| 3 | 2359 | $CO_2$ species | (Al-Wabel et al., 2019) |
| 4 | 1700 | C=O stretch of ketones, aldehydes, 1and esters | (Rong et al., 2020; Tomczyk et al., 2020) |
| 5 | 1609-1632 | C=O stretch in the aromatic rings | (Chen et al., 2022) |
| 6 | 1531 | C=C stretching vibration | (Wang et al., 2020) |
| 7 | 1444-1448 | aromatic C=O and C=C functional groups | (Rong et al., 2020) |
| 8 | 670 | $CO_2$ species | (Al-Wabel et al., 2019) |

**Table S5.** Fitting parameters of XPS C 1s, O 1s, and N 1s spectra in different systems.

| | C 1s | C=C | C-C | C-N | C-O | C=O | C-Na |
|---|---|---|---|---|---|---|---|
| | BE (eV) | 284.00 | 284.63 | 285.62 | 286.85 | 288.50 | - |
| $CBC_{300}$ | Peak area | 31231 | 28899 | 20618 | 5805 | 3167 | - |
| | Percentage (%) | 34.81 | 32.21 | 22.98 | 6.47 | 3.53 | - |
| | BE (eV) | 284.00 | 285.58 | 285.40 | 286.27 | 287.87 | 282.89 |
| $NaCBC_{300}$ | Peak area | 28872 | 44204 | 16100 | 10637 | 9702 | 1747 |
| | Percentage (%) | 25.95 | 39.73 | 14.47 | 9.56 | 8.72 | 1.57 |
| | O 1s | C-O | -OH | C=O | | | |
| | BE (eV) | 531.40 | - | 532.79 | | | |
| $CBC_{300}$ | Peak area | 21004 | - | 32591 | | | |
| | Percentage (%) | 39.19 | - | 60.81 | | | |
| | BE (eV) | 531.24 | 532.08 | 533.15 | | | |
| $NaCBC_{300}$ | Peak area | 16340 | 13669 | 34718 | | | |
| | Percentage (%) | 25.75 | 21.54 | 52.71 | | | |
| | N 1s | -NH | C-N | | | | |
| | BE (eV) | 398.99 | 400.23 | | | | |
| $CBC_{300}$ | Peak area | 1272 | 3698 | | | | |
| | Percentage (%) | 25.60 | 74.40 | | | | |
| | BE (eV) | 398.86 | 400.22 | | | | |
| $NaCBC_{300}$ | Peak area | 1297 | 4260 | | | | |
| | Percentage (%) | 23.34 | 76.66 | | | | |

**Table S6.** Isothermal adsorption fitting parameters of different $NaCBC_{300}$ dosages for MB.

| Dosage | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| (g/L) | $Q_m$ (mg/g) | $K_L$ | $R^2$ | $K_F$ | n | $R^2$ |
| 0.02 | 250.155 | 124.659 | 0.834 | 182.756 | 12.752 | 0.924 |
| 0.04 | 210.865 | 0.941 | 0.781 | 115.613 | 6.321 | 0.994 |
| 0.06 | 174.196 | 3.145 | 0.900 | 113.367 | 6.455 | 0.893 |
| 0.08 | 149.204 | 3.367 | 0.992 | 95.885 | 3.976 | 0.916 |
| 0.10 | 125.210 | 7.043 | 0.963 | 101.537 | 3.459 | 0.950 |

**Table S7.** HOMO and LUMO energy values and other parameters of MB.

| Parameters | Energy (eV) |
|---|---|
| $E_{HOMO}$ | -2.8685 |
| $E_{LUMO}$ | -0.9166 |
| Energy gap ($E_{LUMO}$- $E_{HOMO}$) | 1.9519 |
| Ionization potential (I = - $E_{HOMO}$) | 2.8685 |
| Electron affinity (A = - $E_{LUMO}$) | 0.9166 |
| Chemical hardness ($\eta = (I–A)/2$) | 0.9760 |
| Chemical softness ($\zeta = 1/2\eta$) | 0.5123 |
| Electronegativity ($\chi = (I + A)/2$) | 1.8926 |
| Chemical potential ($\mu = -(I + A)/2$) | -1.8926 |
| Electrophilicity index ($\omega = \mu^2/2\eta$) | 1.8350 |

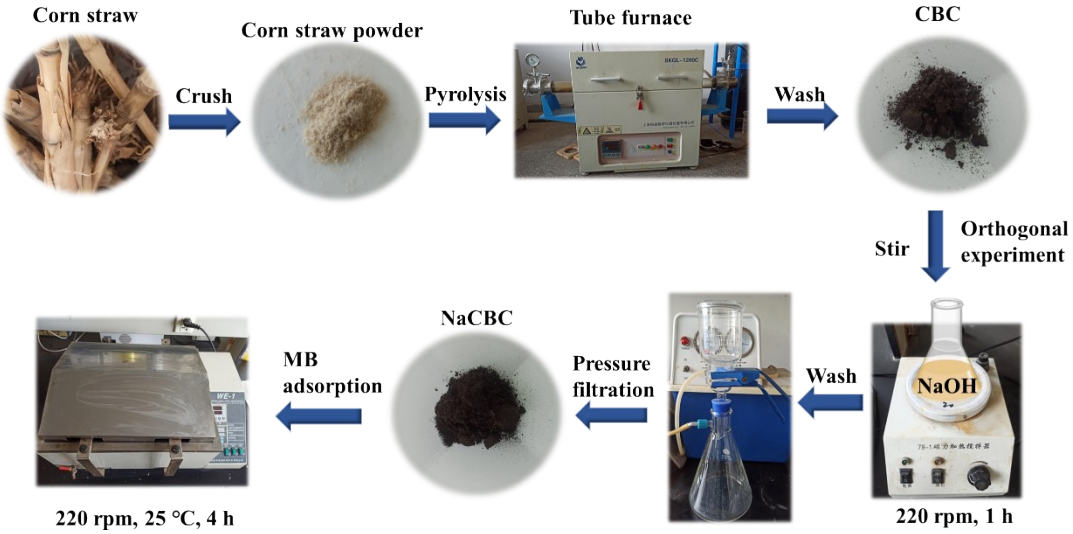


**Fig. S1.** Flow chart for CBC and NaCBC preparation and MB adsorption.

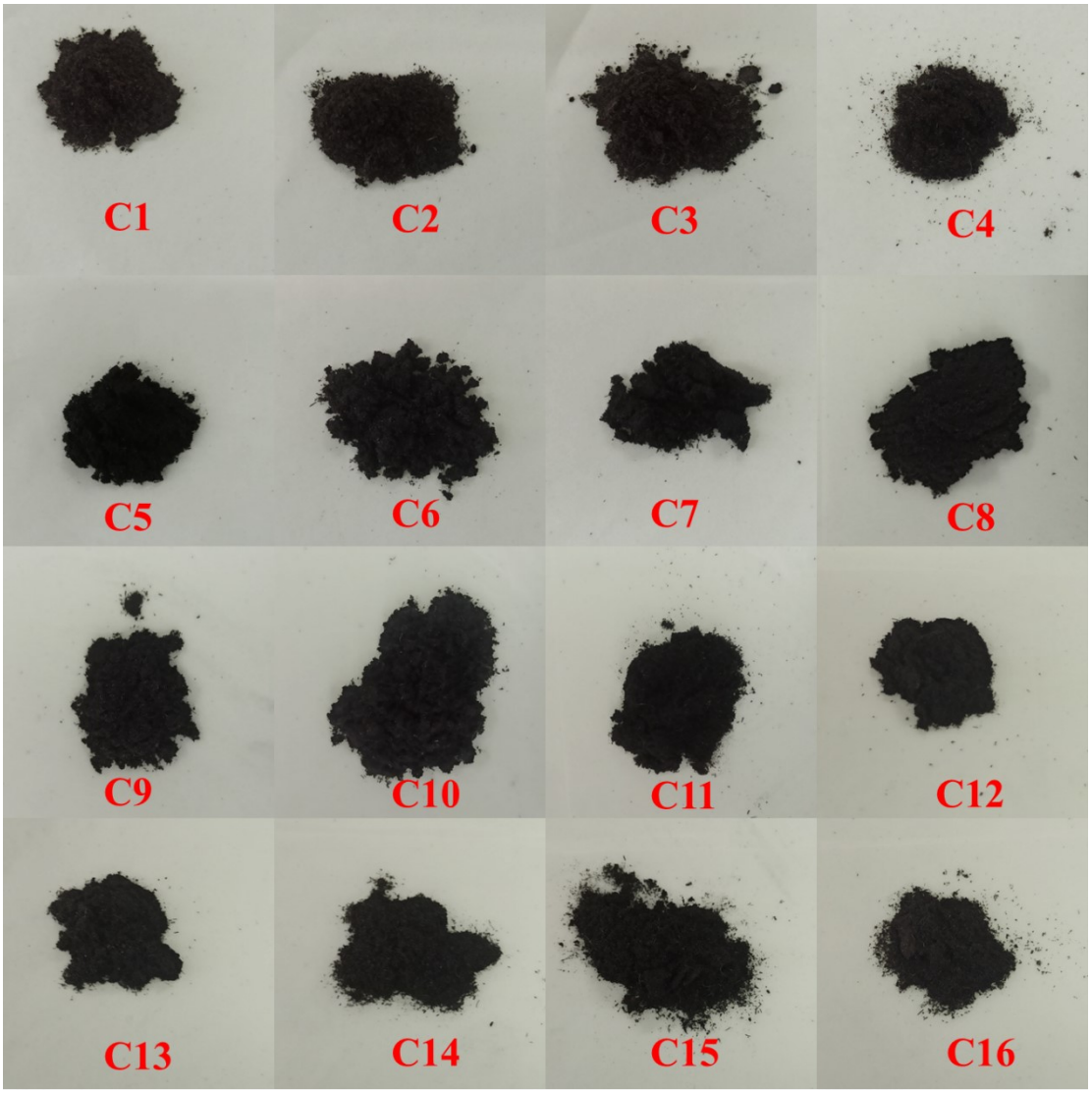


**Fig. S2.** Morphologies of NaCBCs (C1-C16).

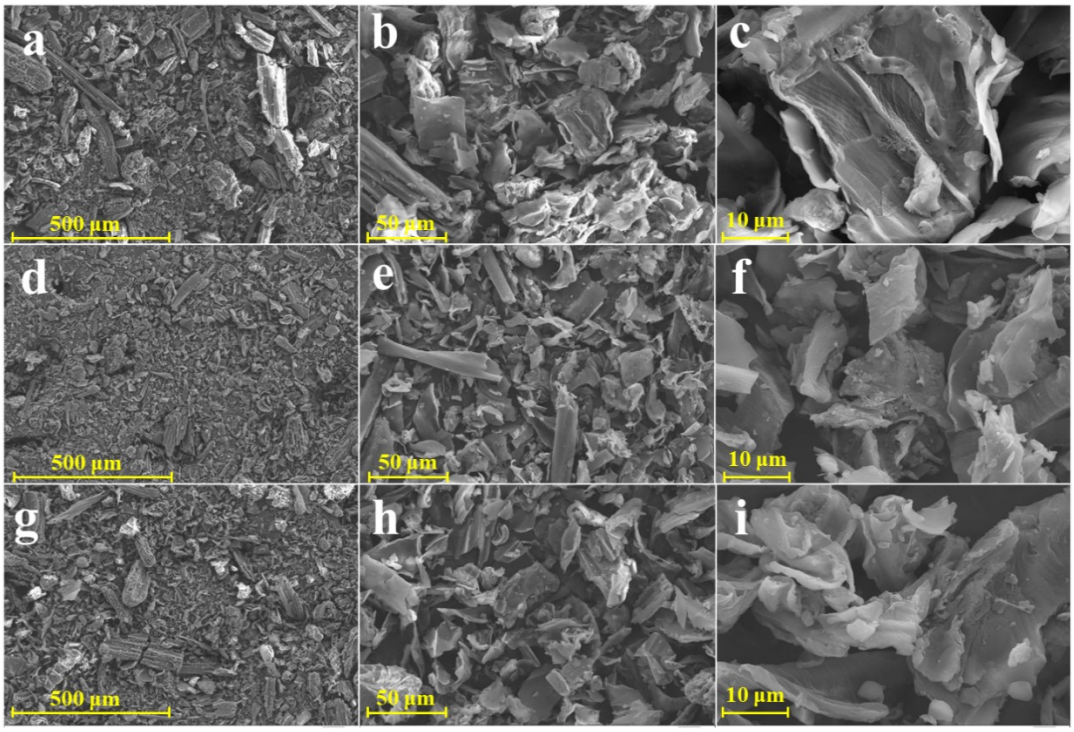


**Fig. S3.** SEM observations of (a-c) $CBC_{400}$, (d-f) $CBC_{500}$, and (g-i) $CBC_{600}$.

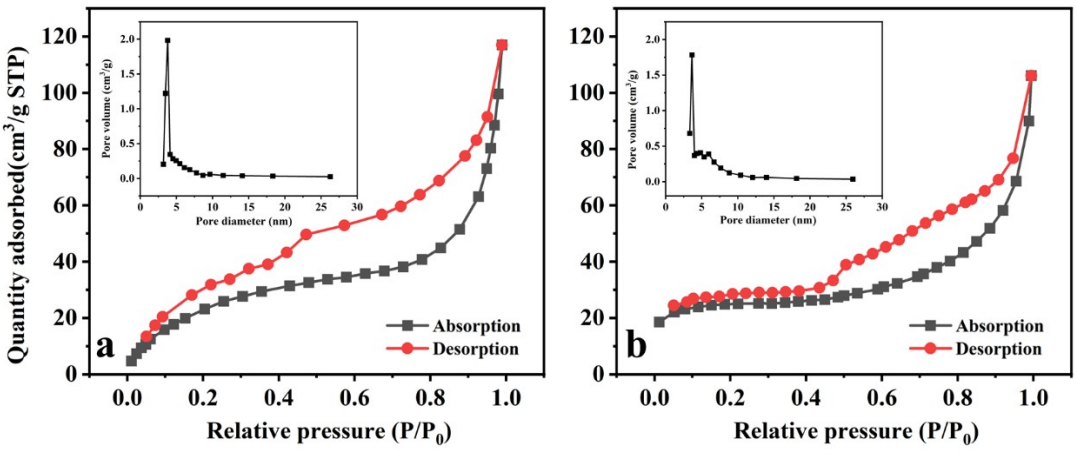


**Fig. S4.** $N_2$ adsorption/desorption isotherms and pore size distribution plots (inset) of (a) $CBC_{300}$ and (b) $NaCBC_{300}$.

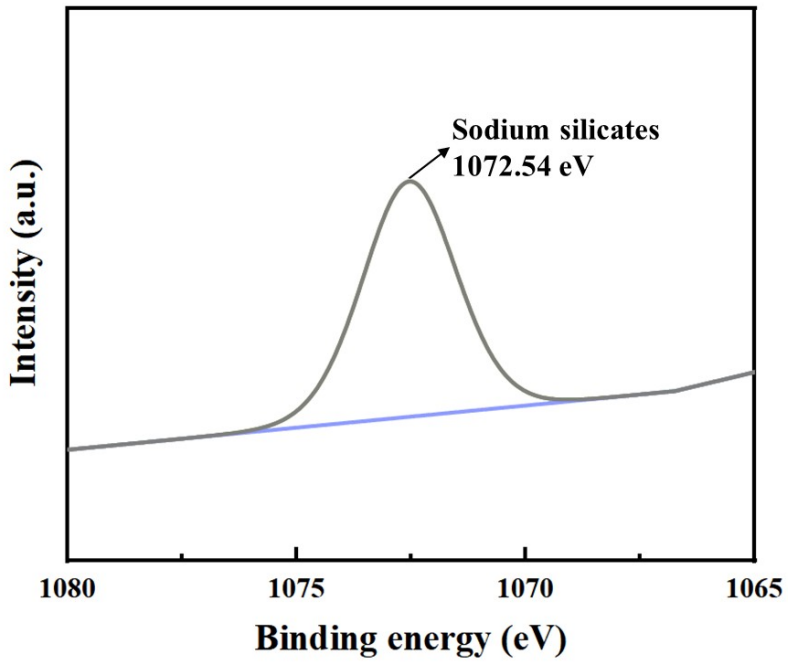


**Fig. S5.** XPS Na 1s spectrum of $NaCBC_{300}$.

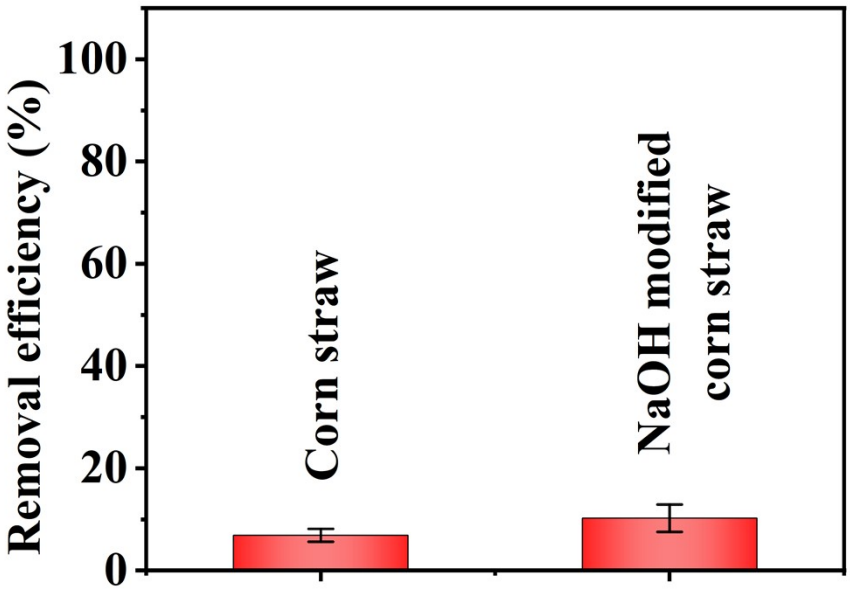


**Fig. S6.** MB adsorption by pristine corn straw and NaOH modified corn straw without pyrolysis.

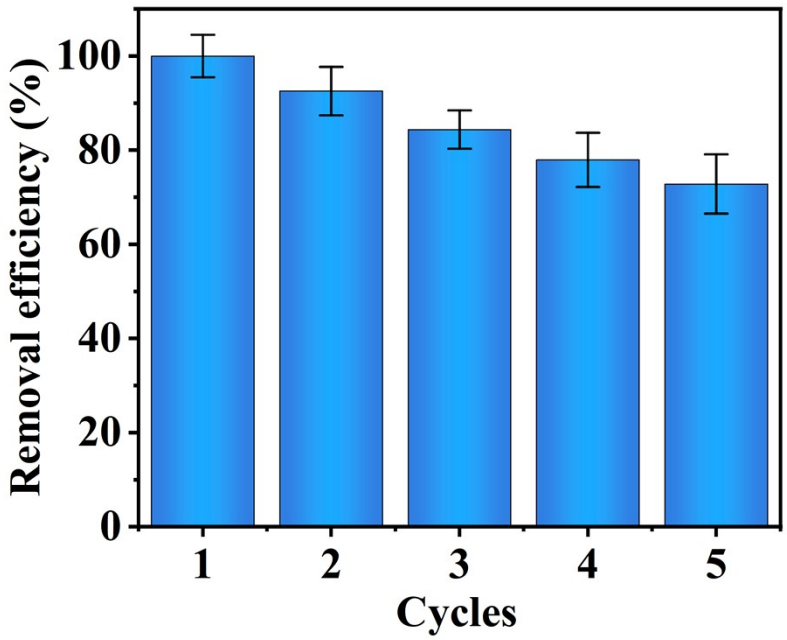


**Fig. S7.** Reusability of $NaCBC_{300}$ for MB removal.

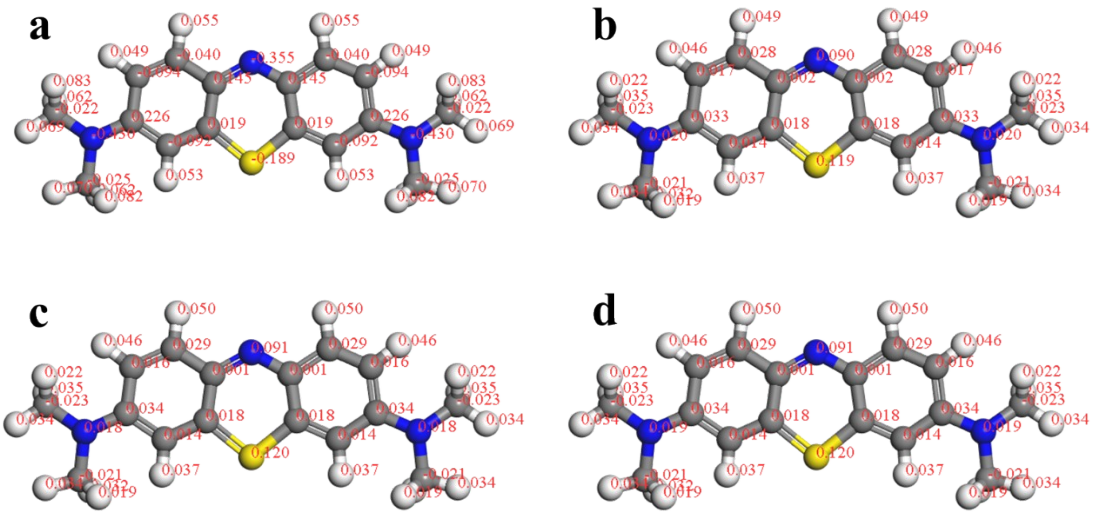


**Fig. S8.** (a) Charge amounts, (b) $f^{-}$, (c) $f^{+}$, and (d) $f^{0}$ of each atom on MB.

# References


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